

# Optical and Color Stability of Aged Specialty Papers and Ultraviolet Cured Ink Jet Prints

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**Abstract.** The present study deals with the optical and color stability of aged specialty papers and ultraviolet cured (UV) ink jet prints. As paper substrates, a fiber synthetic paper and two types of lignin-free papers with included security elements were used. Prints of CMYK color fields using UV Curable Inks were made using a UV ink jet printer, Océ Arizona 250® GT. Samples of papers and UV ink jet prints were artificially aged using standard techniques of accelerated aging, such as moist heat (80°C and 65% RH), dry heat (105°C) and treatment with the a xenon arc lamp (35°C CT, 50°C BST, 35% RH). Aging was performed for periods of 1, 2, 3, 6, and 12 days. In this study, optical properties of untreated and treated paper substrates such as the whiteness and yellowness index and color differences between untreated and treated UV ink jet prints were followed. The tested paper substrates behaved differently. The fiber synthetic paper was more stable than both lignin-free cellulose papers. Some color differences during accelerated aging were observed in prints. The effect depends on the particular ink and type of accelerated aging. On average, dry heat treatment and treatment with the xenon arc lamp showed greater impact on CMYK prints than moist heat treatment. The most stable among the prints was the black ink. © 2010 Society for Imaging Science and Technology. [DOI: 10.2352/J.ImagingSci.Technol.2010.54.6.060402]

## INTRODUCTION

Ink jet prints vary widely not only in the compositions of their colorants and paper but also in their stability. Heat and moisture are two of the most important environmental influences on the stability of color prints and papers. During an aging procedure, the properties of paper materials and ink components can simultaneously change. High temperature and humidity adversely affect all color print materials, although not to the same degree. Such elevated conditions cause the colors to deteriorate quite rapidly. The natural process of deterioration starts as soon as a color image is printed. Also, exposure to light can cause colors to fade and can shorten the life of color prints. The degree of fading varies with the type of illumination and is greater with higher-intensity light.<sup>1</sup> The light fastness of a print depends upon a number of factors, and if not adequate, the color will fade, change chroma or shade, and eventually, the color can disappear altogether. These factors are the exposure conditions, exposure time, substrate and ink film thickness, but primarily, the colorants used. The ink film thickness affects light fastness with thick films being more lightfast due to

greater reflection or light scattering. Resistance to fading or discoloration and durability of printed paper determines its suitability for outdoor applications.<sup>2,3</sup>

The deterioration of paper materials upon aging is initiated by the irreversible breakage of their mechanical, chemical and optical properties. The dry heat aging procedure is very powerful and fast. Three days under these conditions correspond to 25 years of natural paper aging. On the other hand, the moist heat technique of accelerated paper aging is slower and less effective, but simulates the natural aging behavior of paper materials better. Moist heat treatment at 80°C and 65% relative humidity for 24 days is commonly believed to be equivalent to 100 years of natural aging. Another well-known aging technique is the light fastness test, where papers are exposed to artificial sunlight, with one hour of treatment under a xenon lamp corresponding to one day in nature.

Our main research interest is focused on specialty papers, investigation of their properties, printability with digital printing techniques and their durability. In the present paper, the influence of accelerated aging on the optical properties of specialty papers and on the colorimetric properties of specialty papers printed with ultraviolet curing (UV) inks was studied. Previously published research considered mostly the durability of cellulose papers and conventional inks. Havlínova<sup>4</sup> published a detailed study of the stability of offset inks on alkaline offset paper after aging. Vilkman<sup>5</sup> studied the fastness properties of ink jet prints on coated papers. The goal of our research was to estimate the durability of specialty papers and UV ink jet prints for outdoor applications.

## EXPERIMENTAL RESULTS

### Samples

In this study, three types of specialty papers with approximately the same nominal grammage (100 g/m<sup>2</sup>) were used: *Paper 1: Neobond* (Neenah-Lahnstein Co., Germany), *Paper 2: Catenelle* (Fabriano, Italy), and *Paper 3: Small Money* (Gmund, Germany).

Neobond is a durable and hardwearing fiber synthetic paper. This double-side coated paper comprises a mixture of selected pulp and synthetic fibers (polyamide—PA, polyester—PES and viscose), reinforced by a special impregnation.

Catenelle is uncoated paper, made from the 100% el-

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emental chlorine free chemical bleached pulp obtained from wood. The pulp is lignin-free and the stock does not contain ChemiThermoMechanical Pulp or ThermoMechanical Pulp. The paper has a multitonal watermark and contains fluorescent security fibers.

Small Money is a lignin-free paper, made from a mixture of old German marks, waste paper and virgin cellulose fibers.

### Printing

Specialty papers were printed using UV Curable Inks based on pigments produced by Fujifilm Sericol in a flatbed ink jet printer, Océ Arizona® 250 GT (piezoelectric inkjet using Océ VariaDot imaging technology, resolution: 1,440 dpi). The known components of Océ UV Curable Ink, besides its pigments are oxybis(methyl-2,1-ethanediyl)diacrylate, phosphine oxide, 2-hydroxy-4-hydroxyethoxy-2-methylpropiophenone, proprietary multifunctional acrylate R36, and 2-benzyl-2-dimethylamino-4-morpholinobutyrophenone. Océ UV Curable Ink is a fluid with a boiling point/boiling range >100°C, a density of 1.10000 g/cm<sup>3</sup> at 20°C with no organic solvent, a VOC of 0.00%, and is stable up to 50°C.

A printing test form was prepared with cyan (C), magenta (M), yellow (Y) and black (K) solid colors.

### Methodology

The surface properties of specialty papers were tested under standard climate conditions (ISO 187). The roughness and porosity characteristics of papers were measured with a Bendtsen air permeability device according to method ISO 8791-2. Water absorptivity was measured by method Cobb60 (ISO 535).

Specialty papers and CMYK prints were aged using standard techniques for accelerated aging: *Moist heat* based on standard SIST ISO 5630-3 (80°C and 65% relative humidity), *Dry heat* based on standard SIST ISO 5630-1 (105°C) and aging with a *Xenon lamp* based on standard ISO 12040, (35°C Chamber Temperature, 50°C Black Standard Temperature, 35% relative humidity). For determination of the light fastness of papers and prints, a Xenotest® Alpha was used. The apparatus simulates and accelerates the natural weathering process, providing reliable results concerning the long-term behavior of materials. Papers and prints were exposed to different conditions under all three types of accelerated aging for 1, 2, 3, 6, and 12 days.<sup>6-8</sup>

The optical properties of the paper samples were evaluated based on the CIE whiteness and yellowness index YI E313. The measurements were made with a spectrophotometer Spectroflash 600—Datacolor International (D65 standard illumination, 10° standard observer, D/0 measurement geometry and measuring aperture: 2r=6.6 mm).

The CIE formula is based on the calculation of X, Y, Z values. It takes into consideration both lightness and chromaticity of white samples. The CIE whiteness, based on the standard ISO 11475, is defined as

$$W = Y + 800(x_0 - x) + 1700(y_0 - y), \quad (1)$$

where  $W$  is the CIE whiteness,  $Y$  is the tristimulus value of a white sample and  $x$  and  $y$  are the chromaticity coordinates

of the white sample.<sup>9</sup>

The yellowness index, according to the ASTM Method E313, is calculated as follows:

$$YIE313 = \frac{100(C_X X - C_Z Z)}{Y} \quad (2)$$

where  $X$ ,  $Y$ ,  $Z$  are the CIE tristimulus values, and  $C_X$  and  $C_Z$  are coefficients (D65/10°:  $C_X=1.3013$ ,  $C_Z=1.1498$ ).<sup>10</sup>

The colorimetric properties of the CMYK ink were determined using a spectrophotometer, GretagMacbeth Eye-One (D50 standard illumination, 2° standard observer, 45/0 measurement geometry and 4.5 mm measuring aperture). The color differences ( $\Delta E_{ab}^*$ ), which appeared after aging, were calculated according to Eq. (3),

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}, \quad (3)$$

where  $\Delta L^* = L^*(0) - L^*(t)$ ;  $\Delta a^* = a^*(0) - a^*(t)$ ;  $\Delta b^* = b^*(0) - b^*(t)$  are the differences calculated for original (0) inks and the aged inks (t).<sup>11</sup>

## RESULTS AND DISCUSSION

### The Influence of Accelerated Aging on the Optical Properties of Specialty Papers

Specialty papers can be used in many applications, such as identification documents, luggage tags, pressure-sensitive labels, packaging, geological and leisure maps, and educational and visual charts. Typical applications are also in the cosmetics and pharmaceutical industries. A specialty paper is typically one with a specific feature and must have specific characteristics required for a specific use. One of them is synthetic paper. Synthetic paper is defined as a product composed of at least 20% synthetic substances. It can be used in many applications where traditional cotton or pulp based papers will not survive long, for example, where the paper is exposed to the heat, rain and most particularly to UV radiation outdoors. Another kind of specialty paper is one with fluorescent fibers embedded into the paper during manufacturing, watermarks, and other security elements included. Also, for these papers, a higher resistance to heat, moisture, water, and UV radiation is needed in order to last longer than ordinary printing papers.<sup>12-15</sup>

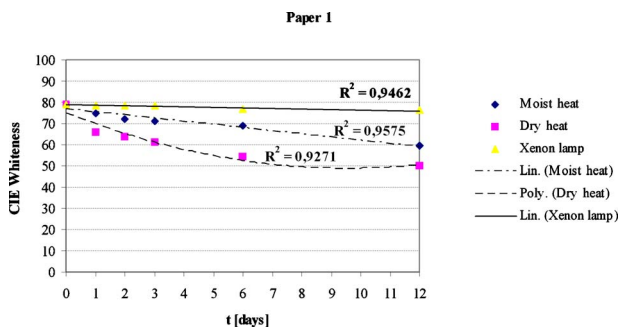
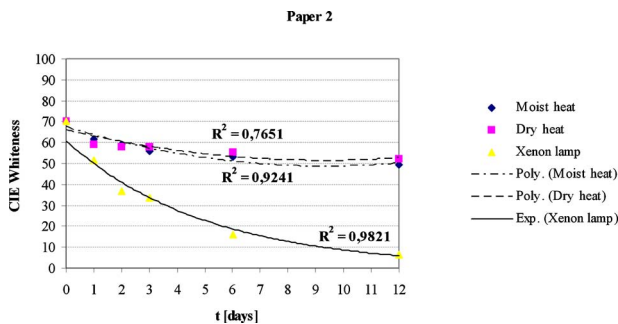
To examine the influence of heat, moisture and light on paper properties, some surface and optical properties of specialty papers were determined. The data are presented in Table I.

In our investigation, three types of accelerated aging were applied, moist heat (80°C, 65% RH), dry heat (105°C) and treatment with a xenon lamp (35°C CT, 50°C BST, 35% RH), in order to determine the durability of synthetic paper and both cellulose and lignin-free papers. The optical stability of specialty papers (i.e., whiteness and yellowness index) during accelerated aging was followed. Figures 1-3 summarize these results.

One of the most significant optical properties of paper is its whiteness. The impression of whiteness consists of the

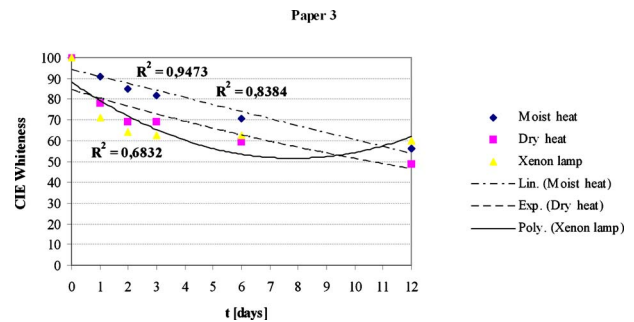
**Table I.** Properties of specialty papers.

| Properties                             | Paper 1 | Paper 2 | Paper 3 |
|----------------------------------------|---------|---------|---------|
| Grammage [g/m <sup>2</sup> ]           | 100     | 90      | 110     |
| Thickness [μm]                         | 112     | 117     | 143     |
| Roughness [ml/min]                     | 630     | 207     | 1575    |
| Porosity [ml/min]                      | 10      | 775     | 120     |
| Water absorptivity [g/m <sup>2</sup> ] | 5       | 8       | 7       |
| CIE whiteness [%]                      | 78.7    | 70.1    | 100     |
| Yellowness index [°]                   | 4.93    | 4.07    | -4.70   |

**Figure 1.** The influence of aging on Paper 1 whiteness.**Figure 2.** The influence of aging on Paper 2 whiteness.

perceived lightness and the hue. The concept of CIE whiteness comprises both the whiteness and tint value of CIE whiteness, the Y value as a measure of lightness and the deviation from neutral. The determined CIE whiteness values for papers before aging are given in Table I. As seen from Figs. 1–3 for all papers, but especially both cellulose lignin-free papers, the highest change in the CIE whiteness was obtained after 24 h of aging, regardless of the treatment applied. With ongoing treatment, the whiteness of all examined specialty papers decreased further.

Papers behaved differently to the applied aging treatments. The most obvious decrease in the CIE whiteness of Paper 1 (Fig. 1) was obtained using dry heat treatment (105°C). After 12 days of treatment, values dropped from 78.7 to 49.9. Treatment with the xenon lamp (35°C CT, 50°C BST, 35% RH), had the smallest impact. Values dropped only for 2.6 units, whereas the moist heat treatment

**Figure 3.** The influence of aging on Paper 3 whiteness.

influenced the CIE whiteness more and a linear decrease was obtained. Paper 2 (Fig. 2) exhibited the lowest stability during treatment with the xenon lamp (values dropped from 70.1 to 6.35 after 12 days) and good stability during the dry heat and moist heat treatment, which is contrary to results obtained for Paper 1. For Paper 3, it was established that the CIE whiteness decreased linearly during the moist heat treatment and exponentially during the dry heat treatment, resulting in a change between 40% and 50% after a period of 12 days. After treatment with the xenon lamp, a 40% decrease was obtained after the third day. Afterwards, the value leveled off. It is obvious that Paper 3, which is made from a mixture of old German marks, waste paper and virgin fibers, is less stable after aging than the other two papers made from chemical pulp (Paper 2) or a mixture of chemical pulp and synthetic fibers (Paper 1). For both lignin-free cellulose papers, the CIE whiteness was least influenced by the moist heat treatment and most influenced by treatment with the xenon lamp, where an obvious change in CIE whiteness was obtained at the beginning of the treatment. For synthetic paper, because of containing synthetic fibers, which are less sensitive to moisture and light than cellulose fibers, the dry heat treatment caused 35% change after 12 days, whereas the moist heat treatment changed the CIE whiteness by only 25% and by none after treatment with the Xenon lamp.

Figures 4–6 show the influence of different aging methods on a paper's yellowness. The tested papers differed slightly in yellowness. Paper 1 (yellowness index YI E313=4.93) and Paper 2 (YI E313=4.07) were more yellowish, while Paper 3 was more bluish (YI E313=-4.70). Paper yellowing is a natural process of paper aging, which is caused by sunlight, moisture, and air. The whole complex of these factors and their impact on paper is called photochemical aging.<sup>16</sup> From Fig. 4, it is seen that accelerated aging has less impact on the fiber synthetic paper (Paper 1) compared to cellulose and lignin-free papers (Paper 2 and Paper 3). Paper 1 yellowness increased polynomially during all three aging methods. After treatment with the xenon lamp, the paper was very stable. Values of yellowness remained almost unchanged after 12 days. Fiber synthetic paper contains a high amount of polyester and polyamide fibers. Polyester (PES) fibers have greater light resistance than polyamide (PA) and cellulose fibers. Photooxidation takes place at higher temperatures.<sup>17</sup> For Paper 1, the change in yellowness was less obvious from the moist heat treatment than from

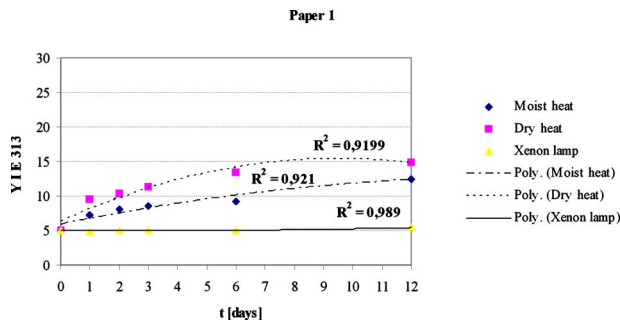


Figure 4. The influence of aging on Paper 1 yellowness.

the dry heat treatment. It is known that synthetic papers are resistant to moisture, which would already damage conventional papers.<sup>12</sup>

The results of all three types of aging show that Paper 2 (Fig. 3) yellowed more slowly during the dry heat treatment, while the treatment with the xenon lamp was the most progressive. After 12 days, Paper 2 obtained a yellowness index YI E313 of 26.51. As with Paper 2, a polynomial increase of yellowness was obtained for Paper 3 too, after all three aging methods. The most obvious increase in yellowness for Paper 3 was obtained by treatment with the xenon lamp first (until the 6th day) and afterwards by dry heat accelerated aging. One of the major sources of decay of materials made from natural fibrous materials such as paper and exposed to environmental stress is the effect of light. It is well known that the paper manufactured from pulp has the tendency to undergo yellowing (brightness reversion) upon exposure to sunlight. Pure cellulose absorbs visible light only to a small extent, while the absorption in the near UV spectral region is more pronounced. Photosensitized degradation, where the energy absorbed by photosensitizers is transferred to initiators, resulting in formation of a reactive species, is the main source of light induced decay of cellulose. The loss of brightness (paper yellowing) during the aging procedure is attributed to the presence of the chromophores formed by the degradation of paper components (cellulose, hemicellulose, lignin). It is believed that, above 90°C, yellowing of cellulose is primarily the result of oxidation.<sup>18–20</sup>

Similar to CIE whiteness, yellowing of papers depends on paper structure and surface coating. Both cellulose papers are very sensitive to light, especially Paper 2, which is uncoated. On the other hand, Paper 2 is very stable to dry heat and moist heat aging, whereas Paper 3, which contains recycled fibers from banknote and waste paper, though it is coated, is much more sensitive to all aging treatments. Paper 1, which is coated and composed also from synthetic fibers, is very stable in light and moisture. Light fastness depends also on coating. A denser coating structure, with smaller porosity, hinders the penetration of light, inhibiting photodegradation. Comparison of roughness, porosity and wettability of specialty papers (Table I) confirmed that lower porosity and surface wettability resulted in better light fastness, as well as better stability of a paper's optical properties to dry heat and moist heat aging.

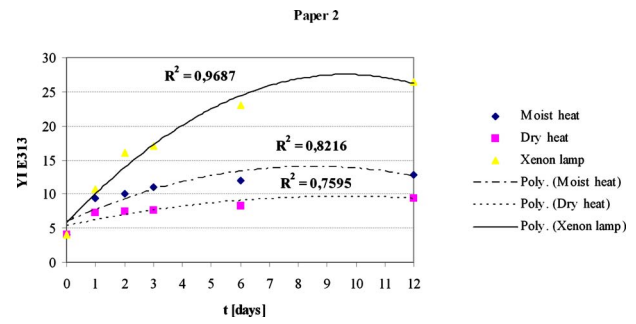


Figure 5. The influence of aging on Paper 2 yellowness.

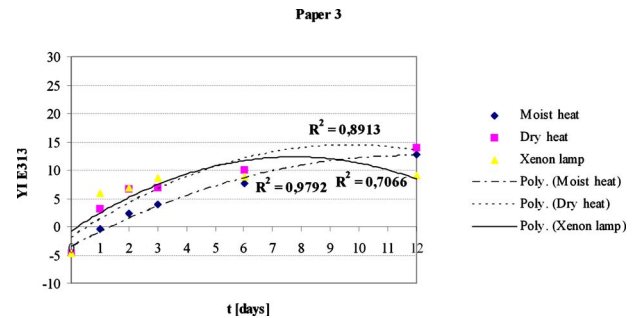


Figure 6. The influence of aging on Paper 3 yellowness.

### Influence of Accelerated Aging on the Colorimetric Properties of UV Ink Jet Prints

Ultraviolet curing inks have a different structure than conventional printing inks. They are made up of monomers, prepolymers/oligomers, pigments/colorants, additives, and photoinitiators/synergists. Ultraviolet reactive inks require high intensity sources of ultraviolet light to initiate a chemical reaction, curing the ink almost instantaneously. Instead of being absorbed into the paper, the UV ink remains on the surface. The UV inks are predominantly used in printing on a variety of substrates, including a range of paper grades, high-grade card products, labels, metal, wood, fabrics, non-absorbent materials such as polyethylene (PE), polypropylene (PP), polyester (PES) etc. These inks are highly durable and resistant to abrasion, which permits their use in harsh environments and where chemical resistance is required.<sup>21–24</sup> One of the advantages of UV inks is also the high light fastness of the cured films. UV ink jet printing is also suitable for outdoor applications, because the UV cured ink films have high durability due to their superior weather resistance.<sup>25</sup>

To examine the fastness properties of UV ink jet prints, solid single color areas were printed on specialty papers. Color difference  $\Delta E_{ab}^*$  was used as a measure of light, moist heat and dry heat fastness, so the CIEL\*a\*b\* values of the prints were measured before and after aging. Differences in the L\*a\*b\* values of CMYK inks after 12 days of aging are presented in Tables II–V, while the influence of accelerated aging on color differences ( $\Delta E_{ab}^*$ ) of CMYK inks printed on all three specialty papers after 1, 2, 3, 6, and 12 days of aging are presented in Figures 7–18.



**Table II.** Differences in  $L^*a^*b^*$  values of cyan ink after 12 days of aging.

| Cyan           |            | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ |
|----------------|------------|--------------|--------------|--------------|
| <b>Paper 1</b> | Moist heat | 1.54         | -2.22        | -1.23        |
|                | Dry heat   | 0.64         | 0.79         | -4.35        |
|                | Xenon lamp | -0.37        | -1.97        | -0.91        |
| <b>Paper 2</b> | Moist heat | 0.07         | -0.73        | -4.20        |
|                | Dry heat   | 0.61         | 0.62         | -6.87        |
|                | Xenon lamp | -0.19        | -2.37        | -1.77        |
| <b>Paper 3</b> | Moist heat | 1.32         | 1.45         | -5.70        |
|                | Dry heat   | 2.06         | 3.26         | -8.75        |
|                | Xenon lamp | 0.79         | -0.80        | -2.14        |

**Table III.** Differences in  $L^*a^*b^*$  values of magenta ink after 12 days of aging.

| Magenta        |            | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ |
|----------------|------------|--------------|--------------|--------------|
| <b>Paper 1</b> | Moist heat | -0.86        | 4.18         | -1.53        |
|                | Dry heat   | -0.86        | 4.25         | -2.79        |
|                | Xenon lamp | -1.06        | 6.15         | -1.37        |
| <b>Paper 2</b> | Moist heat | 0.40         | 1.69         | -1.66        |
|                | Dry heat   | 0.40         | 4.73         | -1.56        |
|                | Xenon lamp | 0.97         | 4.55         | -1.81        |
| <b>Paper 3</b> | Moist heat | 1.07         | 2.97         | -4.44        |
|                | Dry heat   | 1.25         | 2.79         | -4.8         |
|                | Xenon lamp | 1.06         | 4.35         | -3.16        |

**Table IV.** Differences in  $L^*a^*b^*$  values of yellow ink after 12 days of aging.

| Yellow         |            | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ |
|----------------|------------|--------------|--------------|--------------|
| <b>Paper 1</b> | Moist heat | 0.39         | -1.49        | 1.33         |
|                | Dry heat   | 1.44         | -2.33        | -0.30        |
|                | Xenon lamp | 0.58         | -0.52        | 1.91         |
| <b>Paper 2</b> | Moist heat | 1.55         | -1.43        | 4.62         |
|                | Dry heat   | 2.23         | -1.01        | 4.65         |
|                | Xenon lamp | 0.91         | -0.55        | 3.16         |
| <b>Paper 3</b> | Moist heat | 1.66         | -2.53        | 3.77         |
|                | Dry heat   | 2.63         | -3.34        | 3.43         |
|                | Xenon lamp | 1.73         | -0.94        | 4.12         |

Figure 7 shows that the color differences of cyan ink printed on Paper 1 are small after all aging treatments, and that the most stable color was obtained during treatment with the xenon lamp. The total color difference after 12 days of aging was only  $\Delta E_{ab}^* = 2.20$ . During dry heat treatment, the highest color differences were obtained. After 2 days of aging, the color difference exceeded a value of  $\Delta E_{ab}^* = 3$  and ended with  $\Delta E_{ab}^* = 4.47$  after 12 days of aging. The highest

**Table V.** Differences in  $L^*a^*b^*$  values of black ink after 12 days of aging.

| Black          |            | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ |
|----------------|------------|--------------|--------------|--------------|
| <b>Paper 1</b> | Moist heat | -2.48        | -0.04        | 0.13         |
|                | Dry heat   | -2.95        | 0.09         | -0.31        |
|                | Xenon lamp | -2.18        | 0.10         | 0.07         |
| <b>Paper 2</b> | Moist heat | -2.31        | 0.10         | -0.46        |
|                | Dry heat   | -2.84        | 0.06         | -0.30        |
|                | Xenon lamp | -1.78        | -0.06        | 0.09         |
| <b>Paper 3</b> | Moist heat | -0.67        | 0.07         | -0.23        |
|                | Dry heat   | -1.21        | 0.05         | -0.11        |
|                | Xenon lamp | 0.84         | 0.00         | 0.13         |

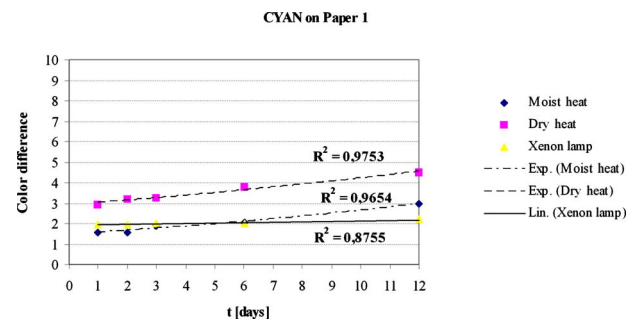


Figure 7. The influence of aging on cyan ink printed on Paper 1.

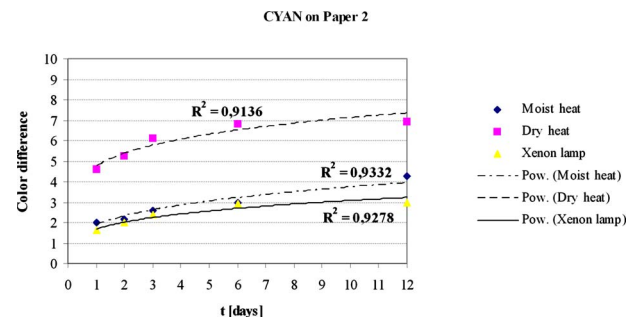


Figure 8. The influence of aging on cyan ink printed on Paper 2.

deviation was obtained in  $b^*$  ( $\Delta b^* = -4.35$ ) as can be seen from Table II.

Significant discrepancies between different accelerated aging treatments were noticed for cyan ink printed on both cellulose and lignin-free papers (Paper 2 and Paper 3). At all treatments, a power law increase in color change was obtained, as seen in Fig. 8. The cyan ink was the most stable in the case of treatment with the xenon lamp. The color difference of cyan ink after 12 days of aging did not exceeded the value of  $\Delta E_{ab}^* = 3$ , which corresponds to a negligible change in color. The dry heat treatment had a significant impact. The color difference started with  $\Delta E_{ab}^* = 4.60$  in the case of one day of aging and ended with  $\Delta E_{ab}^* = 6.93$  after 12 days of aging. The results correspond to massive deviation and significant change in color. For moist and dry heat aging the

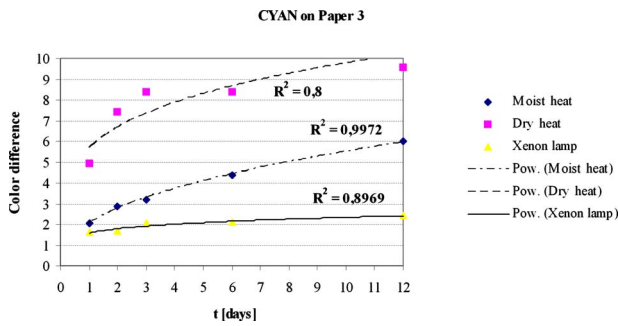


Figure 9. The influence of aging on cyan ink printed on Paper 3.

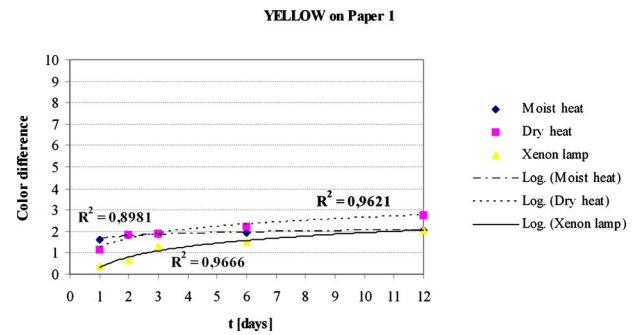


Figure 13. The influence of aging on yellow ink printed on Paper 1.

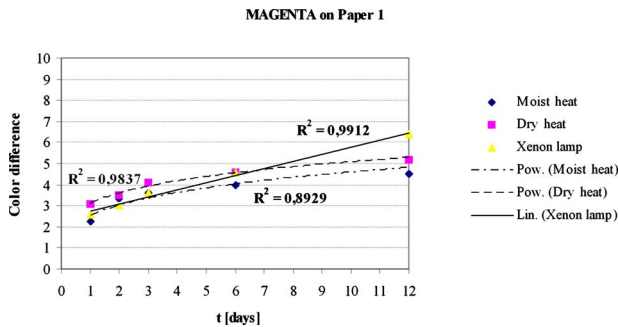


Figure 10. The influence of aging on magenta ink printed on Paper 1.

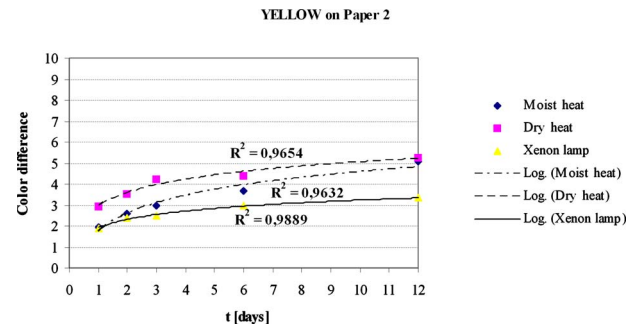


Figure 14. The influence of aging on yellow ink printed on Paper 2.

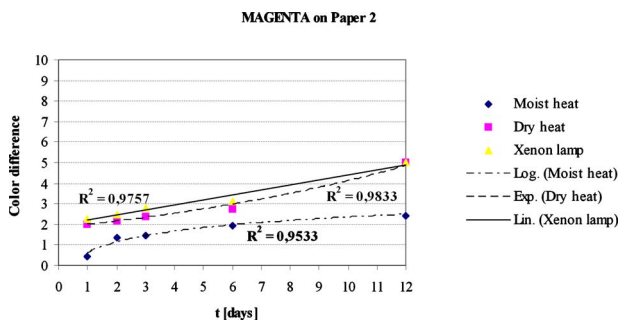


Figure 11. The influence of aging on magenta ink printed on Paper 2.

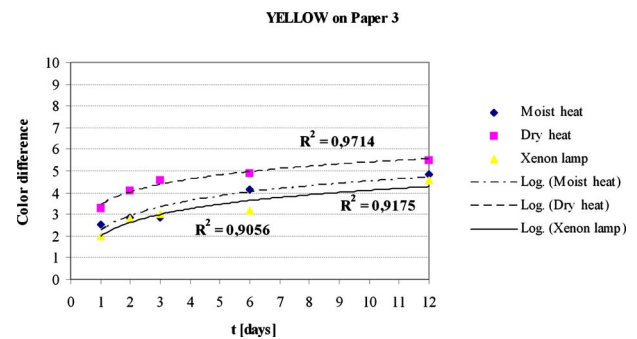


Figure 15. The influence of aging on yellow ink printed on Paper 3.

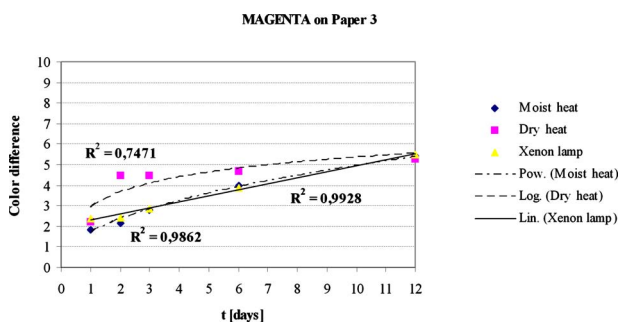


Figure 12. The influence of aging on magenta ink printed on Paper 3.

highest change was obtained for values on the yellow-blue axis ( $\Delta b^* = -4.20$  and  $-6.87$ ), whereas for treatment with the xenon lamp, on the red-green axis,  $\Delta a^* = -2.37$ . The change in the lightness  $\Delta L^*$  for all three aging methods after 12 days of aging was insignificant. Cyan ink printed on Pa-

per 3 was also the most stable after treatment with the xenon lamp and changed the most using dry heat treatment. A power law change in the color differences resulted after 12 days,  $\Delta E_{ab}^* = 9.56$ .

Significant color differences were obtained for magenta ink printed on Paper 1 after all three types of aging. The magenta print became more reddish (Table III). After 2 days of aging the values of color difference reached  $\Delta E_{ab}^* = 3$ . The highest difference was obtained after treatment with the xenon lamp on the print on synthetic paper, where the color difference reached  $\Delta E_{ab}^* = 6.39$  after 12 days of aging (Fig. 10). As shown in Fig. 11 the moist heat treatment did not significantly affect the color of the magenta print on Paper 2. Also, for Paper 1, the change in color was smallest among all three aging treatments. Magenta is more sensitive to dry heat aging in the short period of the treatment (1, 2, and 3 days), as the color change on all three printing sub-

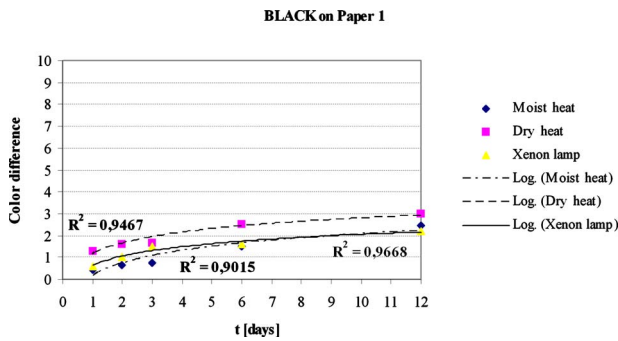


Figure 16. The influence of aging on black ink printed on Paper 1.

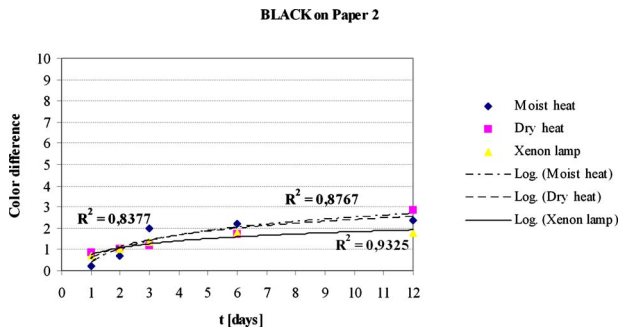


Figure 17. The influence of aging on black ink printed on Paper 2.

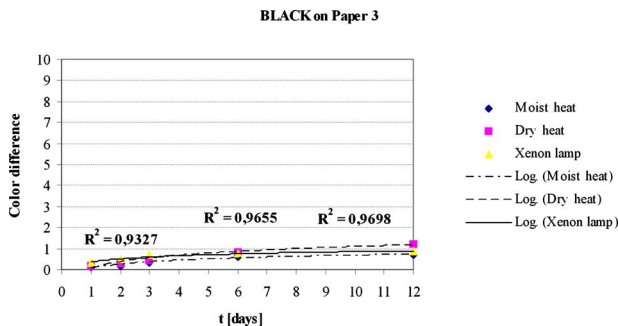


Figure 18. The influence of aging on black ink printed on Paper 3.

strates is higher, compared to the color difference obtained during the other two aging treatments. Additionally, the changes of  $\Delta a^* = 4.73$  for Paper 2 after dry heat and of  $\Delta a^* = 4.35$  for Paper 3 after treatment with the xenon lamp, consequently demonstrated the highest variance of  $\Delta E^*$ . For dry heat treatment, the increase in the color difference followed, for Paper 1 a power law. Paper 2 was exponential and Paper 3 was logarithmic. For Paper 2, after 12 days of dry heat aging, the color difference reached the same value that was obtained after treatment with the xenon lamp.

Yellow ink printed on Paper 1 (Fig. 13) was very stable for all three techniques of accelerated aging. The color differences did not exceed a value of 3, which corresponds to negligible change in color. Application of the dry heat aging method resulted in a significant change in the yellow ink printed on Paper 2 and Paper 3. The color differences obtained for all three aging methods increased logarithmically. After 12 days of aging, the color differences rose to

$\Delta E_{ab}^* = 5.08$  (moist heat),  $\Delta E_{ab}^* = 5.25$  (dry heat), and  $\Delta E_{ab}^* = 3.34$  (xenon lamp) for Paper 2. The color difference of yellow ink printed on Paper 3 (Fig. 15) showed logarithmic increase for all accelerated aging types. The ink was the least stable under dry heat aging. The differences after 12 days were  $\Delta L^* = 2.63$ ,  $\Delta a^* = -3.34$ , and  $\Delta b^* = 3.43$ , which correspond to high deviations.

It is evident from Figs. 16–18 that black ink was very stable for all specialty papers. For all papers, a logarithmic trend line was observed when all treatments were compared. Differences of lightness played the dominant role in the total color difference found for black ink for all three aging types. The color differences were still acceptable even after 12 days. The most stable was black ink printed on Paper 3, where the color difference was approximately 1.

The color difference measured for CMYK inks after 12 days of moist heat accelerated aging are summarized as follows:

(i) The best stability was obtained for the black ink film ( $\Delta E_{ab}^* < 2.5$ ) for all three specialty papers;

(ii) A negligible change was obtained for cyan and yellow ink films on synthetic paper, but a higher difference was observed for the magenta ink film ( $\Delta E_{ab}^* = 4.5$ ) owing to increased  $\Delta a^*$ ;

(iii) Lower stability was obtained for cyan, magenta and yellow ink films on both cellulose papers ( $\Delta E_{ab}^* < 6$ ), mostly because of decreases in  $\Delta b^*$  for cyan ink, decreases in  $\Delta b^*$  and increases in  $\Delta a^*$  for magenta ink and increases in  $\Delta b^*$  and  $\Delta L^*$  and decreases in  $\Delta a^*$  for yellow ink.

UV cured ink films have no barrier to moisture or water. Their resistance to the influence of moisture varies depending on how they key on paper substrates, which is influenced by the roughness and wettability of the paper surface. The poorer the keying to the substrate, the more critical are the conditions under the influence of moisture.<sup>26</sup>

The color differences measured for CMYK inks after 12 days of dry heat accelerated aging are summarized as follows:

(i) The best stability was obtained for the black ink film ( $\Delta E_{ab}^* < 3$ ) for all three specialty papers;

(ii) A negligible change was obtained for yellow ink film on synthetic paper, and a still acceptable but higher difference was found for cyan and magenta ink films ( $\Delta E_{ab}^* = 4.5$  and 5.2) resulting from a decrease in  $\Delta b^*$  and, for magenta ink, also from an increase in  $\Delta a^*$ ;

(iii) A color change between 5 and 5.5 was obtained for magenta and yellow ink films on both cellulose papers, for magenta ink because of differences in  $\Delta b^*$  and  $\Delta a^*$ , and for yellow ink because of increases in  $\Delta L^*$ ;

**Table VI.** Differences in optical density of CMYK inks after 12 days of aging.

|                |            | $\Delta D_C$ | $\Delta D_M$ | $\Delta D_Y$ | $\Delta D_K$ |
|----------------|------------|--------------|--------------|--------------|--------------|
| <b>Paper 1</b> | Moist heat | 0.04         | 0.06         | 0.01         | 0.05         |
|                | Dry heat   | 0.04         | 0.05         | 0.00         | 0.02         |
|                | Xenon lamp | 0.03         | 0.09         | 0.02         | 0.01         |
| <b>Paper 2</b> | Moist heat | 0.03         | 0.05         | 0.01         | 0.03         |
|                | Dry heat   | 0.06         | 0.08         | 0.01         | 0.07         |
|                | Xenon lamp | 0.07         | 0.09         | 0.05         | 0.06         |
| <b>Paper 3</b> | Moist heat | 0.08         | 0.05         | 0.00         | 0.05         |
|                | Dry heat   | 0.05         | 0.02         | 0.00         | 0.04         |
|                | Xenon lamp | 0.09         | 0.09         | 0.02         | 0.06         |

(iv) Cyan ink films on cellulose papers demonstrated significant change in color,  $\Delta E_{ab}^* = 6.9$  for Paper 2 and 9.5 for Paper 3, mainly because of substantial decreases in  $\Delta b^*$ .

Because dry heat treatment is the most powerful aging technique, it is not surprising that, after 12 days, the change in color is higher compared to moist heat treatment. Besides ink properties, surface properties of paper influence the stability of ink films.

The color differences measured for CMYK inks after 12 days of accelerated aging with the xenon lamp are summarized as follows:

(i) The best stability was obtained for the cyan and black ink films ( $\Delta E_{ab}^* < 3$ ) for all three specialty papers;

(ii) A negligible change was obtained for yellow ink film on synthetic paper too, whereas for magenta ink, a significant increase in  $\Delta a^*$  resulted in a higher color difference ( $\Delta E_{ab}^* = 6.4$ );

(iii) For both cellulose papers, a negligible change was obtained in the cyan ink films, but a higher difference was noted for yellow ink films ( $\Delta E_{ab}^* < 4.5$ ) because of increased  $\Delta b^*$ . A difference ( $\Delta E_{ab}^* > 5$ ) for magenta ink films was observed, where input of  $\Delta a^*$  and  $\Delta b^*$  was evaluated, but mostly increases in  $\Delta a^*$ .

Accelerated aging with the xenon light, which simulates the light fastness of papers exposed to daylight for approximately 9.6 months, resulted in lower changes in color compared to the other two aging techniques. Also, with this technique, some influence from paper surface structure on color stability was noticed. However, the light fastness appears to be dependent on the specific colorant-paper interactions.

In Table VI, the differences in optical density for CMYK inks after 12 days of aging are presented. Only a small reduction in relative optical density was obtained. Among all inks, the magenta ink film on all three specialty papers exhibited the lowest stability during aging; a decrease of up to

7% was obtained. On cellulose papers, the highest loss was caused by treatment with the xenon lamp for all four inks, and also for magenta and yellow inks on synthetic paper. The optical density of ink film on paper is influenced by paper characteristics and pigment concentration in the ink. The paper roughness and porosity influence the formation of ink film on the paper surface, its thickness and consequently its stability during aging. Because we cannot obtain information on the composition of the inks used in our study, we cannot identify the chemical processes initiated by accelerated aging methods.

## CONCLUSIONS

Different standard techniques of accelerated aging (moist heat, dry heat, and treatment with a xenon lamp) were applied in the stability investigation of optical properties of specialty papers and colorimetric properties of UV ink jet prints. The results obtained during processes of accelerated aging indicated that the CIE whiteness of papers decreased, and yellowness increased. The application of treatment with the Xenon lamp caused the most obvious decrease of whiteness for Paper 2 (lignin-free paper with multitoneal watermark and fluorescent security fibers); while for Paper 1 (fiber synthetic paper), the lowest influence was noticed. Paper 1 yellowed more during dry heat treatment, while Paper 2 and Paper 3 (lignin-free paper made from mixture of old German marks, wastepaper and virgin fibers) yellowed more during treatment with the Xenon lamp. The higher stability of synthetic paper during aging can be explained with the higher stability of synthetic fibers (PES and PA) to light and moisture in comparison to cellulose fibers. Substantially higher light fastness in synthetic paper is also the consequence of a surface coating, which acts as a protective layer.

All three types of accelerated aging used in this study give some information about color stability and are equally useful for all samples analyzed. The reduction in the optical density of CMYK ink films on all specialty papers after 12 days of accelerated aging was small, the highest being in magenta ink. Dry heat accelerated aging and treatment with the xenon lamp caused higher differences in color than moist heat aging. The lowest heat-fastness was obtained for cyan ink and the lowest light-fastness was for magenta ink film on all specialty papers. The most stable was black ink. Every printed color reacted differently to the process of aging, where different parameters (i.e., paper characteristics, ink composition) seem to be involved in the destructive process. UV ink jet inks behaved differently on different types of papers based on the composition of papers and their surface properties. The results from our study lead to the following conclusion: the best optical stability was attained for fiber synthetic paper, and the best color stability under heat, moisture, and light was shown by black ink.

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