# Aging Properties of Non-Impact Prints : Influence of the Paper Properties

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## Abstract

With the large and rapid development of digital printing, arose the problem of aging properties of the corresponding printed materials, such as : light fastness, moisture and heat resistance.

In the present work, a special emphasis is put on the role played by the nature of the paper itself in these fastness characteristics.

Four selected ink-jet papers were analyzed : chemical composition of the surface, permanence properties. Then, ink-jet prints on these papers were analyzed after accelerated aging. The experimental parameters were time of exposure to UV-light, humidity and temperature.

The fastness properties were evaluated in terms of color differences, but also by microscopy observations and spectroscopic analyses.

The results obtained showed, among other things, the significant influence of the paper properties on the global aging performances of the prints.

## Introduction

Images produced by ink jet technology can be affected by light, humidity, heat, and many other factors.

Rapid fading of the ink-jet inks is commonly observed and often reported (1, 2, 3, 4, 5, 6).

Light fastness has been one of the most intensively studied properties of ink jet prints, especially over the last 2-3 years (1). Several authors, recommend a holistic approach of media, ink, head design, colorant, better than considering each alone. As a matter of fact, the interaction of the media with the dye can alter the light fastness of an ink et print by up to 100 fold (1, 2, 3, 4).

Sargeant et al. (4) have studied the rate of fading of different ink-media systems. They showed that the rate of fading on cellulose media is strongly ink-dependent. They also noticed that for some inkjet media and ink combinations, the colors initially fade, and then revert, within relatively short exposure times. It suggests the presence of competitive reaction pathways in the color fading process.

Lavery et al. (3) have also studied the ink/media interactions in the context of light fastness. They described the effect of some important factors, such as :

- media pH, which may favour one form of the colorant or the pigment, and also affect the solubility of a dye, which are pH dependent,
- surface coating nature : the majority of the polymers used in this context are very good at absorbing the ink vehicle and have limited effect on the photo stability of the image, but some coating layers can significantly reduce the photo stability of dyes.
- location of the colorant : the porous surface layer can help to protect the chromophore from light degradation. The light fastness can also be improved by increasing the diffusion of the colorant into the surface coating layer.

Steiger and Brugger (2) concluded that no single, well-defined mechanism can explain the photo-degradation of ink-jet dyes in prints. They even observed different mechanisms of dye destruction can occur in the same receiving layer. the environment of the colorant has a strong influence on the stability of the chromophore to light"

Combination of dye agglomeration and photochemical mechanism of degradation of pigment or dye may occur.

Different reaction pathways may occur : photo-oxidation or photo-reduction, dependent on the chemical environment of the dye.

Moreover, in the same context, one can notice that agreed standard for light fastness of ink jet print are still needed.

## Materials and Methods

Four high-quality ink-jet papers were analyzed : two uncoated papers (HRP and EQP) and two coated papers (GP and PGP). Their morphological properties were described in a previous work. Their optical properties (gloss, reflectance and fluorescence) were measured before aging experiments.

Cyan, Magenta, Yellow and Black solids were printed on the different papers, with an EPSON Stylus printer with the same settings and the same set of ink jet printing inks.

### *Light fastness tests*

The unprinted papers and the printed samples were exposed to a xenon light for 72 hours, in a Xenotest. The samples were placed on a rotating carousel, ensuring uniform exposure. The light was filtered through a system of IR and UV filters, which simulated a sunlight exposure. The relative humidity and the temperature were monitored. An evaluation of the aging was made each 24h.

Two experimental conditions were tested :

30°C, 50 %HR, during 72 h

and 30°C, 76 %HR, during 48 h.

One hour of exposure in the laboratory conditions corresponds approximately to 20 hours of exposure to daylight.

### *Dark aging*

In order to simulate an accelerated aging, unprinted and printed samples were also placed in a heated oven (105°C) for 48 hours. This treatment necessarily leads to a severe degradation of the mechanical properties of the papers, but only the optical changes are studied in the present work.

## Measurements : aging evaluation

The effect of the aging experiments on the unprinted papers was evaluated by spectrophotometry in the CIELa*b* 1976 system, with an X-Rite SP62 spectrophotometer (D/0° geometry, D65 illuminant, and 10° observer, specular included), by IR spectroscopy and gloss measurements (60°). In addition, a "yellow index" $Y_i$ and a "white index" $W_i$ of the papers was calculated before and after aging experiments, according to formulæ (1) and (2) :

$$Y_i = 100.(1 - 0.85Z/Y) \qquad (1)$$

$$W_i = 100 + 800.(x_n - x) + 1700.(y_n - y) \qquad (2)$$

where : *X, Y and Z* are the CIE tristimulus values,

*x and y* the trichromatic coordinates, defined by :

$x = X/(X + Y + Z)$ and $y = Y/(X + Y + Z)$

$x_n$ and $y_n$ being the trichromatic coordinates of the illuminant (here, D65/10° : $x_n = 0.314$ and $y_n = 0.331$)

The effect of aging on the printed samples was evaluated by spectrophotometry with the color difference ΔE, obtained from (3):

$$\Delta E = [\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}]^{1/2} \qquad (3)$$

where $\Delta a^*$, $\Delta b^*$ and $\Delta L$ are the differences between $a^*$, $b^*$ and $L^*$, respectively , before and after aging.

## Results and discussion

### 1. General observations

UV-light exposure led to a drastic alteration of the colors, whatever the substrate, which was expected and is often described for this type of print, but large differences exist between the papers. These disparities in behavior are illustrated on Figures 1a, b and c, which presents the color shifts due to UV-light exposure, in a ($a^*$, $b^*$) diagram.

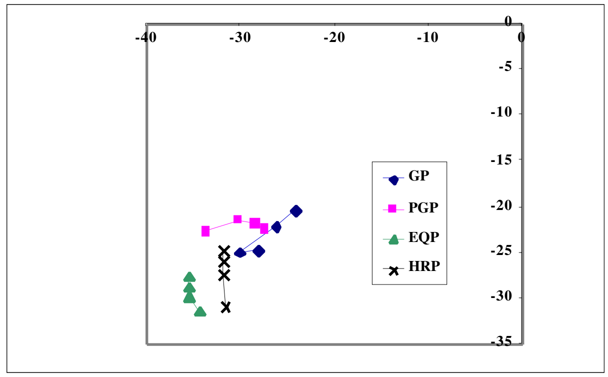


*Fig.1a*

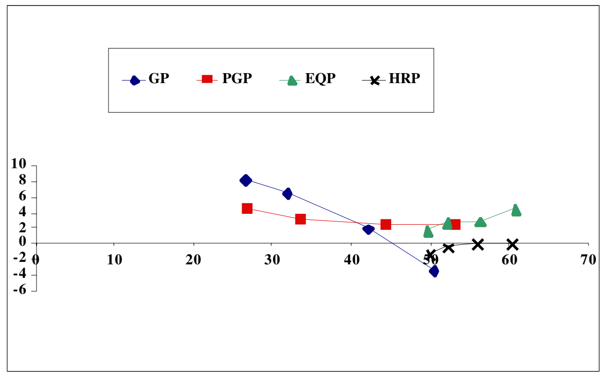


*Fig.1b*

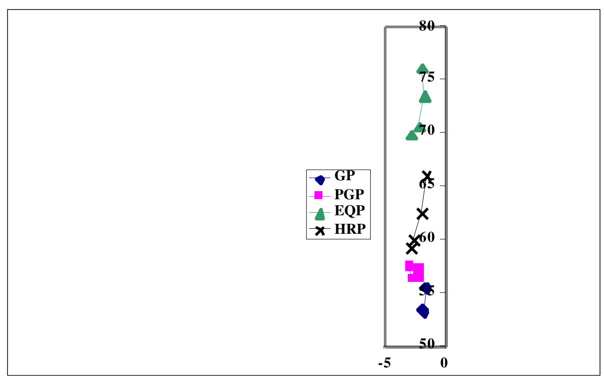


*Fig.1c*

*Figure 1a, 1b and 1c, (a*, b*) diagrams of Cyan, Magenta and Yellow solids, printed on papers GP, PGP, EQP and HRP.*

In addition, the gloss of the coated papers and of the corresponding prints was strongly affected by UV-light exposure. Table 2 gives the 60° gloss values for the papers before and after exposure. These results were corroborated by scanning electron microphotography, shown on Figure 2. The polymers of the coated layer on these papers contains in their molecules chromophoric moities which make them sensitive to direct photolysis, leading to a degradation of the surface of the coating. The consequences are a drop of gloss, and an supplementary change of the resulting color, in addition to the color degradation due to the intrinsic properties of the inks.

**Table 1. Gloss of papers**

| | Before exposure | After exposure |
|---|---|---|
| HRP | 2.9 | 2.8 |
| EQP | 2.5 | 2.5 |
| GP | 83.6 | 23.9 |
| PGP | 86.7 | 68.1 |

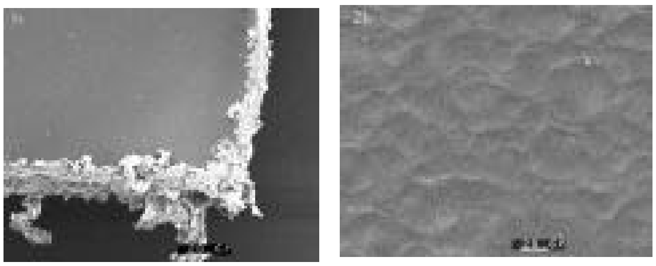

*Figure 2: SEM micrographs (x 350) of the surface of paper GP before (2a) and after (2b)UV-light exposure.*

On the contrary, the dark aging (in oven at 105°C) did not affect strongly the colors, excepted for Cyan, which will be discussed later.

## 2. Permanence properties of the papers

The four papers possessed a certain degree of fluorescence, obtained by fluorescent whitening agents in their composition. This fluorescence was evaluated from the reflectance values at 457 nm, measured with and without UV light.
Table 2 gives the results expressed as a percentage of the light reflected by the paper at 457 nm, due to the fluorescence.

**Table 2. Fluorescence of papers**

| | Fluorescence ratio (%) |
|---|---|
| UC1 | 64.6 |
| UC2 | 19.5 |
| C1 | 20.6 |
| C2 | 20.6 |

Fluorescent whitening agents have generally a poor light fastness and heat resistance. They degrade relatively rapidly, which was visible on the reflectance spectra of the papers after aging experiments, presented on Figures 3a and 3b, for EQP paper. This effect was different according to the papers, which may explain the disparities in the aging behavior of an ink/paper system.
The effect of aging in darkness was essentially a decrease in brightness, which was more gradual than the corresponding degradation after UV exposure. The yellowing of the papers was characterized by the variations of $Y_i$ and $W_i$. The results are presented in Table 3.

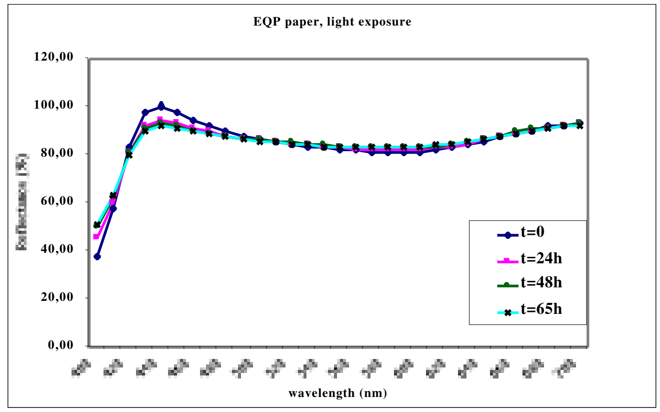


*Figure 3a, Reflectance spectra of EQP paper, before and after light exposure.*

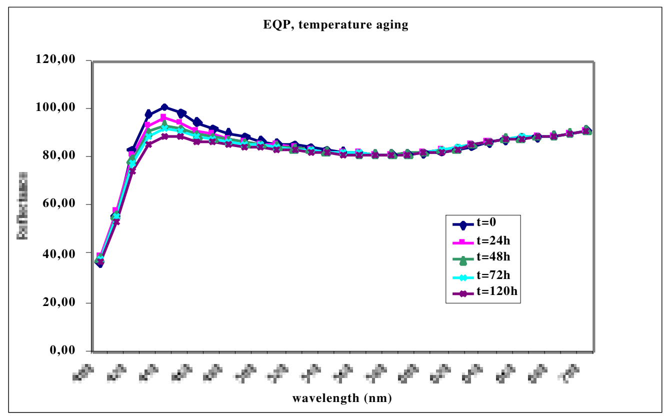


*Figure 3b, Reflectance spectra of EQP paper, before and after dark aging (heat exposure).*

**Table 3. Dark aging : variations of $Y_i$ and $W_i$ after 72h in oven.**

| | $Y_i$ initial | $Y_i$ | $W_i$ | $W_i$ |
|---|---|---|---|---|
| HRP | < 0 * | 15.1 | 124.3 | 79.1 |
| EQP | < 0 * | 6.1 | 130.1 | 109.2 |
| GP | 5.5 | 14.1 | 110.9 | 83.3 |
| PGP | 5.7 | 11.1 | 110 | 93.3 |

* high degree of fluorescence

The samples were also submitted to the same exposure conditions, with higher humidity. The results showed that humidity did not change drastically the final reflectance of the papers, which was not expected.

## 3. Consequences on the printed samples

As shown in the first observation, the media permanence properties have direct consequences on the resulting aging behavior of the prints. But the final result is also ink-

dependent, as it is a complex combination of ink and paper interactions.
For example, after UV-light exposure, the color shifts for magenta ink were much larger than the corresponding degradation of the other colors (see Fig. 1), which is due to the intrinsic properties of this colorant, but was emphasized by the nature of the coated media. This suggests that the molecules of the coating layer, and their degradation, promote the photo-degradation of the magenta pigments and dyes used in the ink formulation. On the contrary, the yellow colors were more affected on the uncoated printed papers. For Cyan, the paper nature had no influence in this context. These comments are resumed by the ΔE values presented in Table 4.

**Table 4. ΔE values of printed colors – papers**

| | Cyan | Magenta | Yellow |
|---|---|---|---|
| HRP | 6.5 | 13.4 | 7.0 |
| EQP | 4.2 | 14.5 | 6.5 |
| GP | 6.1 | 29.6 | 0.9 |
| PGP | 6.3 | 30.9 | 2.0 |

The cyan samples were more affected by dark aging, which is explained by the important yellowing of the papers in these conditions. This phenomenon is characterized by a loss of reflectance in the 400-500 nm region of the spectrum (see Fig. 3b), which is also the region where the reflectance of Cyan is maximum, which explains why this color was more affected than the others.

## Conclusion

This study emphasizes the influence of the paper properties on the global permanence properties of an ink-jet printed document. This points on the fact that the choice of the type of paper is fundamental, and is at least as important as the choice of a set of inks. It was also useful to evaluate the aging degradation with different indexes. This study is one step towards a better understanding of the fading mechanisms of different colorants on any given media. However, difficulties remain to anticipate the final result of degradation of one ink/paper combination.

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## Biography

Anne Blayo graduated from the French Engineering School of Papermaking and Printing in 1988 and received her Ph.D. at the National Polytechnique Institute of Grenoble in 1994. Her thesis concerned rheological properties of printing inks. Since then, she has been working in the French Engineering School of Papermaking and Printing as a teacher and searcher. Her work is focused on printing inks (chemical composition, physico-chemical and rheological properties) and color-related studies.