Contribution of Spectroscopic Techniques to the Analysis of Permanence Properties of Ink-Jet Printed Materials

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Abstract

The demand for image permanence properties has increased with the development of ink-jet applications. Depending on the ink composition, the nature of the colorants (pigments or dyes) and the media properties, very different results can be obtained. The effect of the ageing experiments are frequently assessed in terms of color differences (ΔE) and gloss variations.

The objective of this paper was to evaluate, in addition to these measurements, other techniques of analyses, such as UV-visible, IR and Raman spectroscopies.

Two different ink-jet papers have been tested with two ink-jet inks (pigment- and dye-based inks) before and after UV-light expositions.

Not only the analytical techniques used allowed to evaluate the extent of the permanence properties of the samples, but they also made possible to interpret with a better accuracy the physico-chemical origin and the mechanism of the possible degradation.

Introduction

Lightfastness has been one of the most studied properties of ink jet prints. Several authors recommended a holistic approach of media, ink, head design, better than considering each separately. For example, the interactions between the colorants and the media can modify the photo-degradation of the dyes, or pigments.[1-4] Moreover, the conditions of aging introduce many other factors, which have a strong influence on the final result : relative humidity, temperature, other pollutants (ozone,…).

In most of these studies, the evaluation of the fading is made by the measurement of color and gloss differences. Colorimetric measurements (such as L*a*b* values and color differences calculations, ΔE) give interesting results, regarding the visual perception of the color difference, induced by the fading of colorants. But they do not give any precise signification on the origin of this shift.

Recent studies report the use of spectroscopic techniques as instructive and reliable methods to analyze the fastness properties of ink jet prints.[5,6]

These studies demonstrate that FTIR and Raman spectroscopies allow to get a better insight into the physico-chemical interactions. They also underline the fact that difficulties remain in creating reliable aging tests.

One of the crucial difficulties is to define all the conditions of laboratories aging, as many factors may influence the global result.

The objective of this work, which follows a previous paper,[7] was to test the efficiency of IR, UV-vis and other spectroscopic techniques to evaluate the lightfastness of ink jet prints.

Materials and Methods

Samples

Patches of the four pure primary inks (Cyan, Magenta, Yellow and Black) were printed on a photo-quality paper, with an Epson Stylus Printer (soluble-dyes based inks).

The purity of these solid colors was obtained by printing directly from a Postscript file, in order to avoid the generation of other dots, which could create some catalytic fading. Catalytic fading may happen when one dye can transfer its absorbed energy to another dye at lower energy level.[8]

Lightfastness Tests

The paper 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. All these experiments were made at 35°C and 30% RH.

An evaluation of the aging was made after different times.

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

Analysis Aechniques

1. UV-vis Spectroscopy

This spectrometer (UNICAM UV Series 300) gives the transmission spectrum from 325 to 900nm of liquid samples placed in quartz cells. Water was taken as the reference liquid.

2. Reflective Spectrophotometry

***Spectrophotometer Colourtouch*:** this spectrophotometer, which is commonly used by paper makers, gives the reflective spectrum of a sample, with the possibility to filter the incident light under 420nm. Thus, with this apparatus, an evaluation of the contribution of the fluorescence is possible. The analyzed surface is a disc of 4 cm diameter.

***Sphere Spectrophotometer X-Rite SP62*:** this spectrophotometer gives the reflective spectrum of a sample, between 400 and 700 nm, by 10nm steps. The analyzed surface is a disc of 0.8 cm diameter.

3. FTIR Spectrometry

Transmission as well as reflection IR-spectra were obtained on the Perkin-Elmer FTIR (Paragon 1000) spectroscope.

***Transmission*:** liquid samples were analyzed between two NaCl faces. Powder samples were ground with KBr.

***Reflection*:** the reflective spectra of printed samples were obtained with an ATR bench.

Results and Discussion

1. Contribution of the Paper to the Aging of the Prints

In our previous study, we already noticed a large effect of the fluorescence of the papers. Many inkjet papers contain fluorescent whitening agents, in order to enhance their apparent whiteness.

Fluorescent whitening agents have generally a poor lightfastness and heat resistance. They degrade relatively rapidly, which is visible on the reflectance spectra of the paper after aging experiments, presented on Figure 1.

The Colourtouch measurements gave, by difference, the contribution of the fluorescent agents (Figure 2) in the reflectances of the paper after different exposure times.

This contribution has an influence in the range of wavelength from 420 to 560 nm. In this domain, the variations of the reflectance factor of the paper with the time of exposure can be modeled according to the equation (1).

$$R_\infty(t, \lambda) = R_\infty(0, \lambda).exp(-\mu(\lambda).t^{\alpha(\lambda)}) \qquad (1)$$

where:

λ is the wavelength (nm),

t is the time of exposure to light (hour)

α and μ are constants which depend on the material

Given this result, it may be interesting to analyze the reflectance spectra of printed samples, in order to evaluate the extent of the influence of the fluorescence in the global alteration of the print.

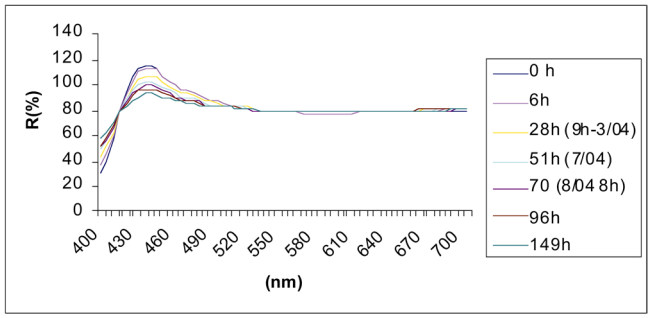

Figure 1. Reflectance spectra of the paper (fluorescent agents are activated by the incident light)

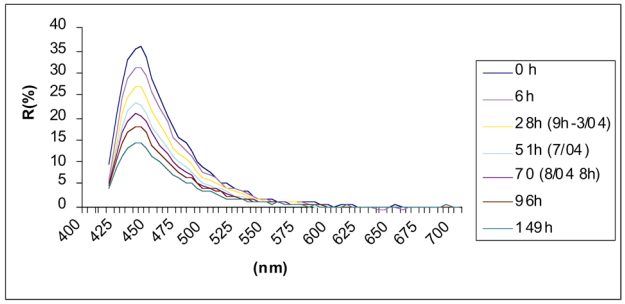

Figure 2. Contribution of the fluorescent agents to the variations of the reflectance spectrum of the paper

Figure 3 shows the reflectance spectra of the magenta ink printed on the paper, after different exposure times, including the fluorescence of the paper. On this figure, it is difficult to analyze the fading of the magenta colorant alone in the low wavelength region (400- 500 nm).

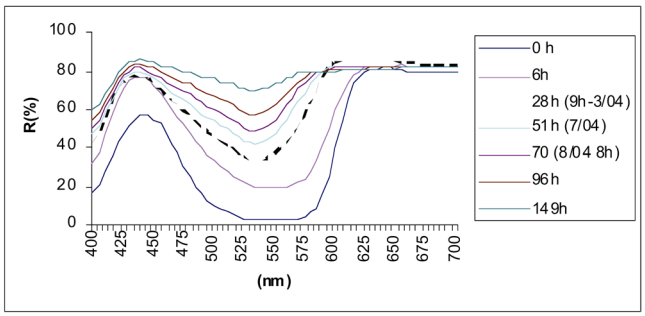

Figure 3. Reflectance spectra of printed magenta (fluorescent agents are activated by the incident light)

On Figure 4, the contribution of fluorescence has been removed, which permitted to make a separate analysis of the magenta ink behavior on the whole visible spectrum.

The alteration of the magenta colorant followed a model similar to equation (1).

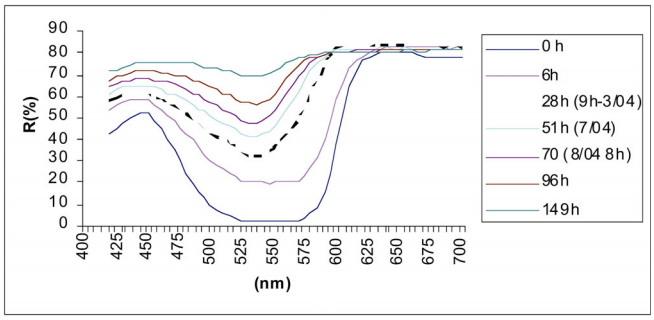

Figure 4. Reflectance spectra of the printed magenta (fluorescent agents are not activated)

2. Contribution of the Ink to the Lightfastness Analysis by UV-vis Spectrometry

The lightfastness of the inks was studied by UV-spectrometry. Inks, in the quartz cells at suitable dilution in water, were placed in the Xenotest. After a 24h exposure, no change were observed on the UV-vis spectra.

This result was unexpected, regarding the rapid fading of the same inks on the paper.

In fact, the mechanisms of photo-degradation are based on photo-oxidation, and/or photo-reduction of the chromophores (especially in the case of azo colorants). These reactions could not take place in the cell as quickly as in an air exposure.

For example, in the case of magenta ink, the addition of a hydrogen donor or a hydrogen acceptor in the ink immediately led to a rapid shift of the absorption peak at 565nm in the UV-vis spectrum, which confirmed the modification of the colorant.

This short experiment shows that the lightfastness of the ink must be studied in the presence of air, at least in conditions similar to those of the ink on the paper.

Moreover, this suggests that the dyes or pigments of the ink will behave differently depending on the way they are protected from air, after printing.

Other experiments were conducted on the same ink, spread on a glass plate. The plate was placed in the Xenotest, and the result was analyzed after different aging time, with the X-Rite spectrophotometer. The evolutions of the reflectance spectra are shown on Figure 5, and confirm the results obtained on the liquid ink analyzed by UV-vis spectroscopy, after the addition of hydrogen acceptor.

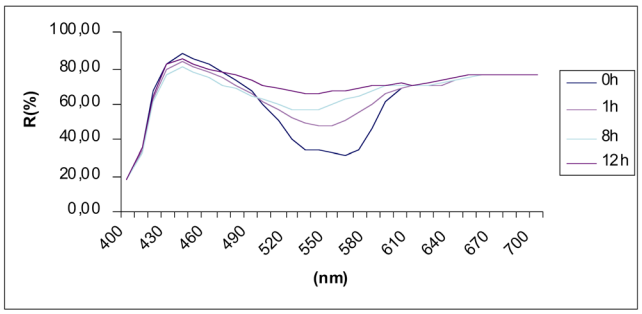

Figure 5. Evolutions of the reflectance spectra of magenta ink placed on a glass plate

3. Analysis of the Printed Samples, After Extraction, by IR-Spectrophotometry

FTIR spectroscopy was also used to assess the fading of ink-jet inks on the paper.

After printing, samples were submitted to UV-light, as described previously. The ink was then extracted with suitable solvent, and then analyzed by FTIR spectroscopy.

This type of analysis gave qualitative information on the modification of the structure of the colorant after UV-light exposure, although the characteristics of –N=N- are not clearly detectable on IR-spectra. The RAMAN spectroscopy gave better results in this context, which has also been demonstrated by Vikman.[5]

Conclusion

Spectroscopic techniques, such as FTIR and UV-vis, are very commonly used in analytical chemistry area, and still seldom explored in the context of printed samples analysis. However, this short study, which presented some preliminary results, gives an idea on the possibilities of such analyses.

For example, the separation of the contribution of the various elements (paper components, ink colorants…) gives information, which is necessary, before analyzing their mutual interactions. This was shown in our case in the analysis of the contribution of whitening agents in the paper.

Another aspect of interest, in this context, is the possibility of fine analysis, which may lead to the comparison between documents.

The outlook of such study is undoubtedly that further investigation towards other complementary techniques is necessary, in order to enhance the understanding of the aging mechanisms of prints.

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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.