# Permanence of Ink-jet Prints: A Multi-Aspect Affair

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## Abstract

Light stability of ink jet prints has since the early beginnings of this technology been one of its most reticent problems. It has been one of the major reasons why ink-jet prints have not been used more widely, particularly not in the display market. Only in more recent times, systems have come onto the market which allow the exposure of such prints in- and outdoors for reasonable periods of time. Permanence of the printed image is a function of the image receiving layer. It can be shown that single elements used in the construction of the layer do either alone or in combination with others profoundly influence the stability of the image. Permanence is, however , to an even greater extend a function of the inks used. It has been recognised for quite some time that the dyes used in formulating inks play the major role. Only little is known about the role solvents or solvent combinations play in light stability. The stability of an image is moreover a function of the type of light to which it is exposed. Some ways and means to improve and influence light stability will be described. It is also the aim of this paper to show that the permanence of the printed image is the result of an optimised fit of receiving media and inks.

## Introduction

With the proliferation of ink- jet printing into more and more areas of imaging, the question of print permanence, archival and preservation become very important. Ink-jet prints are about to partially substitute photos or screen prints in such diverse application as trade show displays, home photo, light box and point-of sales displays and signage.

The cited applications have very different requirements on print stability. As these applications were traditionally a domain of photo, it made sense to try to predict the life expectancy of new technologies as ink-jet by using similar methods and tools as were used to predict the life expectancy of photo prints and films for display.

## Factors in Light Permanence

With the increasing permanence of ink-jet prints, it becomes impossible to do real time tests for most of the media and ink development work. As is the case for photo, accelerated aging methods have to be used, with all the uncertainties that originate from compressing the time scale of degradation from years and tens of years to several days or weeks.

The international community of photo manufacturers and related industries have developed a standard (ANSI IT9.9-1990 or ISO 10977) that describes the basic procedures for light fastness testing and accelerated light fastness testing. It can be applied to ink-jet prints with certain restrictions. The standard regulates

- the proper preparation of samples
- general properties of the test equipment
- five different light exposure and environmental conditions (simulated outdoor sunlight, incandescent room light, fluorescent room light, simulated indirect daylight, intermittent tungsten lamp slide projection)
- necessary features of the test image
- properties and data to report

It also gives the background for the extrapolation method and experimental evidence for photo prints.

The light fading of images is a very complex process and is by no means only dependent on the total light exposure. In this paper we used the ANSI IT 9.9 standard test and real time outdoor exposure to investigate internal and external influences that contribute to the fading of ink-jet prints. Internal factors are the receiving layer and its components and dyes and other ink components, external factors are temperature, type of light and exposure, humidity and the print pattern. Unless stated otherwise the results given refer to the simulated indirect daylight exposure conditions.

## Role of Ink Receiving Layers on Permanence

The characteristic of the ink receiving layer is an important parameter in the control of the light fading processes. The chemistry of the organic polymer or the mineral forming layer, the nature of the additives, the layer structure as well as the layer surface properties allow for an optimisation of the permanence performance in modern "micro-engineered" multi- layer design.

The mechanism of the photo degradation of imaging dyes was investigated for ink receiving layer of various compositions. Depending on the nature of the dye either reductive or oxidative mechanism were detected. As measured by spectrophotometry, the dye aggregation in the layer plays an important role in the light fading performance.

### Matrix composition

To illustrate the effect of the film forming matrix on the physical and redox properties of the receiving media, transparent binary mixture of gelatin and various polymers (A-F) were coated and printed with a commercially available printer and ink (HP 660).

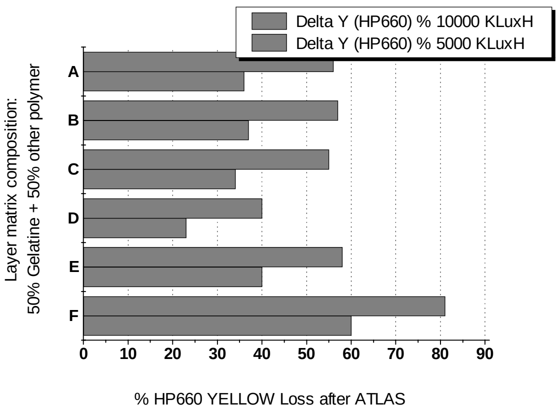


*Figure 1: Matrix effect of gelatin / polymer A-F (1:1) binary film on light fading of the Y colour in HP660 prints*

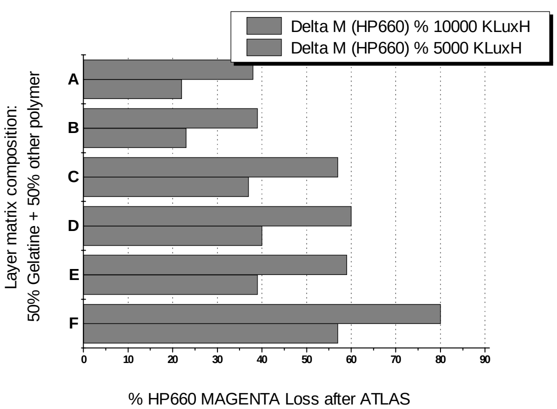


*Figure 2: Matrix effect of gelatin / polymer A-F (1:1) binary film on light fading of the M colour in HP660 prints*

The results shown in figure 1 to 3 indicate a strong influence of the matrix on magenta while much reduced for yellow and cyan (pure colour). When looking at composite black differences become again much larger.

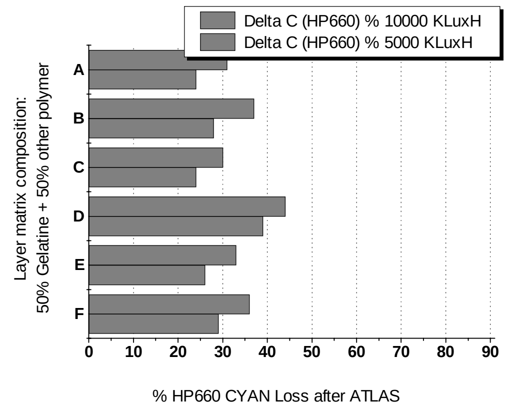


*Figure 3: Matrix effect of gelatin / polymer A-F (1:1) binary film on light fading of the C colour in HP660 prints*

### Additives

The influence of various additives were investigated: antioxidants, reducing compounds, peroxide scavengers, triplet quenchers, etc. Complex effects were detected. Understanding of these additives is of primary importance for the control of photo-catalysis, i.e. different dye degradation behaviour whether the dye is alone or in a composite colour.

### Multi-layer structure

With the capability to coat multi-layer structures various, even incompatible additives, can be incorporated into one receiving layer to provide different functionalities as shown in figure 4.

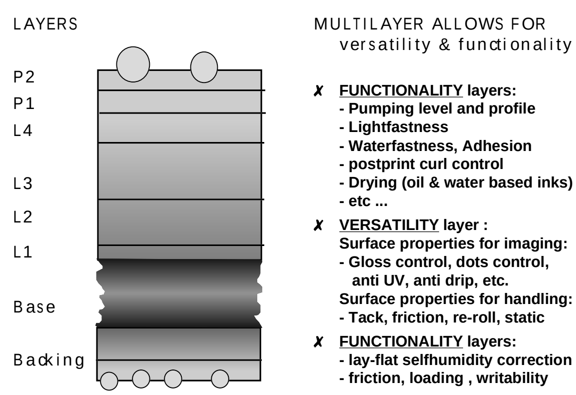


*Figure 4: Ink-Jet photographic concept: Micro-engineered multi-layers*

Versatility and functionality can therefore be separated in the design. As an example, additives controlling light fastness can be incorporated at a position, where they do not interfere with other properties such as surface gloss, etc. Likewise, aggregation promoting compounds can also be located in suitable layers and thus favour in-situ nanopigment formation.

## Influence of Inks on Image Permanence

The ink composition has an enormous influence on the permanence of the final image. Certainly the most important element of an ink contributing to image stability are the dyes. Needless to mention that also the formulation and in many cases specific additives play an important role in determining permanence.
How do inks contribute to permanence?
The major ink factors influencing permanence are:

- Dyes
- Ink formulation
- Environment

**Dyes**

In recent times, an intensive search for light fast dyes took place with most major dye producers. Phtalocyanines have since some time been identified as a class of stable cyan dyes. For quite some time, several yellow dyes with fair to good stability were available. Therefore, stability of the cyan and yellow dyes has often not been the limiting factor towards permanent images. No adequate, really light fast magenta and black dyes were foreseeable. This is one of the reasons why much activity was invested by several companies in the development of inks based on pigments. In many applications pigments are known for their light stability. Pigmented inks therefore still seem to be the clamour word in the industry when it comes to light fastness. Based on many years of experience in designing water-soluble, diffusion fast dyes for the ILFOCHROME ® silver-dye-bleach photographic system, known for its permanence, we at Ilford have chosen to investigate the way of water-soluble dyes. We were able to develop a set of water-soluble YMCK dyes with excellent properties. From the onset of this work the ultimate goal was to reproduce hue and stability of photographic images with inks based on these dyes.

Light fastness is directly related in several ways to the structure of the dye. It depends primarily on the chemical structure of the chromophor but also, and probably less known, it depends on the structure of the auxiliary groups. This can best be demonstrated for the case of magenta dyes. The best magenta dyes are to be found within the class of azo dyes. Even within that class the differences are enormous. A typical example illustrating the effect of the structure is shown in figure 5

In the early days of ink jet printing, textile dyes and often many other „off-the-shelf dyes“, initially meant for quite different applications, were used to formulate inks. This allowed for only restricted possibilities in designing inks. Only when dyes were specifically synthesised for ink jet applications proper ink development became possible. At the time, little consideration was given to the fact that the value of a particular dye for ink jet printing is equally dependent on the auxiliary groups as it is on the chromophor.

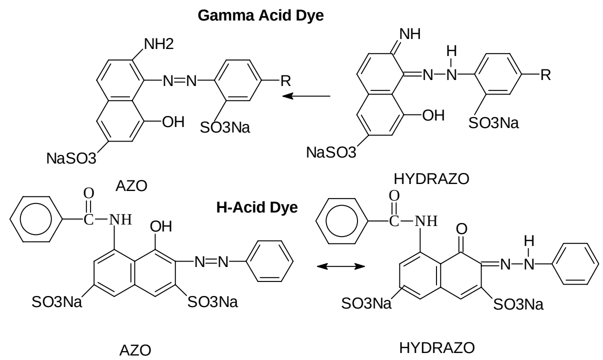


*Figure 5: Gamma Acid Dyes: Light stable, less brilliant; H-Acid Dyes: Less light stable, brilliant*

In general the difficulties are two sided. On the one side highly water-soluble dyes are needed to achieve a maximum of freedom in formulating the ink to perform at their best on the printer and to be stable over many years. On the other side dyes are asked for which, once in or on the receiving layer are water fast, that is practically not water-soluble anymore. This difficulty can to a great extend be solved if dyes are available which aggregate in a controlled manner. This is were judiciously chosen auxiliary groups come into play. These groups are designed in such a way to impart maximum solubility of the dye in an aqueous solution but the very same groups should not interfere with dye-aggregation once the dye is in its solid state. Good solid aggregates are what imparts permanence to a water-soluble dye. This is the point were dyes meet pigments. Organic pigments achieve their light fastness due to their particle forming properties. However, once fine enough to pass the nozzles of modern print heads and fine enough to begin to match the colour space of dyes they begin to lose their inherently better light stability. Small particles are easily attacked by light. Such small particles tend to converge to the same size as good dye aggregates. One point which has not received enough consideration as yet is the fact that dyes do potentially interact among themselves, with in many cases strongly negative effects on permanence. Such interactions can sometimes be explained via triplet sensitised photo-oxydation. This kind of phenomenon is particularly pronounced in dye mixtures containing phtalocyanines where this dye acts as a sensitiser causing the fading of the second dye in the mixture.

Since the structure not only determines the permanence of the dye but to a large extend also other properties like colour and hue and in particular image quality, the final selection of a dye is always at best a compromise.

**Ink Formulation**

The effect of the formulation upon the quality of the printed image is well known. It is common knowledge that parameters like print density, black shade, print uniformity, drying time and print head performance among others are profoundly influenced by the choice of solvents and additives used in formulation oft the ink. Apart from the dyes, the major elements of an ink used for thermal ink jet printing are the organic solvents, in general called humefactants. Besides helping to solubilise the dyes their major task is to keep the ink from drying on the nozzles. Preoccupation with parameters related to printer performance and image quality tend to overshadow the strong influence precisely theses solvents can have on the permanence of the printed image. There are different ways how solvents can interfere with permanence: The more important factors are the influence on aggregation/desegregation of the dye, then also the effect on the equilibrium between the azo / hydrazo forms in azo dyes (see figure 5). Solvents can moreover act as sensitizers producing energy rich reactive species causing the dyes to fade. Solvents can be decomposed by irradiation producing decomposition products responsible for dye fading.

A typical example demonstrating the influence of a related series of solvents on the stability of a particular magenta dye is shown in figure 6**.**

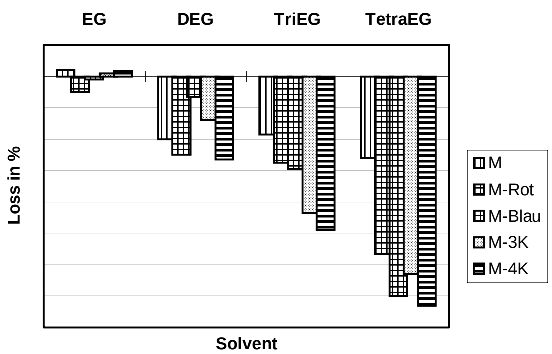


*Figure 6: Loss in % of initial dye density after 10000 kluxh of exposure. Influence of the solvents / humefactant on the permanence of a magenta dye.*

## The Influence of the Environment

Among all the environmental factors, the amount of light, the duration of the exposure is one of the most determining parameters in fading, but the spectral composition of the light ( UV/no UV, Fluorescent / incandescent) and the sample humidity can play a very important role as well. This is often overlooked when accelerated light fading is done with UV lamps and under dry conditions. Reliable predictions of fading for real indoor or outdoor displays are not justified based on UV light data alone.

The following graphs demonstrate the quality of the predictions of the accelerated fading test against real outdoor exposure and should show some of the environmental factors influencing light stability. The test equipment used was an Atlas Ci-35 weatherometer which runs with a regulated humidity of 40% r.h. and with day/night cycles. A light cycle of 3.8 hours is followed by a dark cycle of 1 hour. It takes about 120 hours total time to achieve the exposure of $10^4$ kluxh. For the outdoor exposure, samples were mounted on the roof of a building in Switzerland at an angle of 90° for 20 days in early summer with no further weather protection as the laminate.

The graphs show the percentage losses in dominant colour density compared to the unexposed sample. Given are the losses in density of the primary colours C,M,Y and K as well as the losses in process black (Y,M,C black) and 4K black (Y,M,C,K black) after an exposure of $10^4$ kluxh. Large bars mean large losses in colour and correspond to a weak light stability of that colour.

While fading is quite reproducible if done under controlled exposure kluxh (kilo lux hours), the average person prefers to know the number of months or years that a print can be exposed before fading is visible. The above statement bears two problem areas, namely when is fading visible and what will be the exposure at a certain display location over time. Both questions are discussed in (1) .
Figure 7 contains the results of ink A on two different media ( I and II) both protected by the same encapsulation laminate. Encapsulating laminates protect against humidity, but not against UV light.

Figure 7a shows the fading generated by the accelerated fading equipment. Figure 7b shows the same ink/media/ laminate combination after 20 days of real outdoor exposure

Figure 7c plots the percentage losses in density for ink A on media II, again encapsulated. Figure 7d contains the outdoor fading data. The correlation between the experimental fading and the real outdoor exposure is very good.

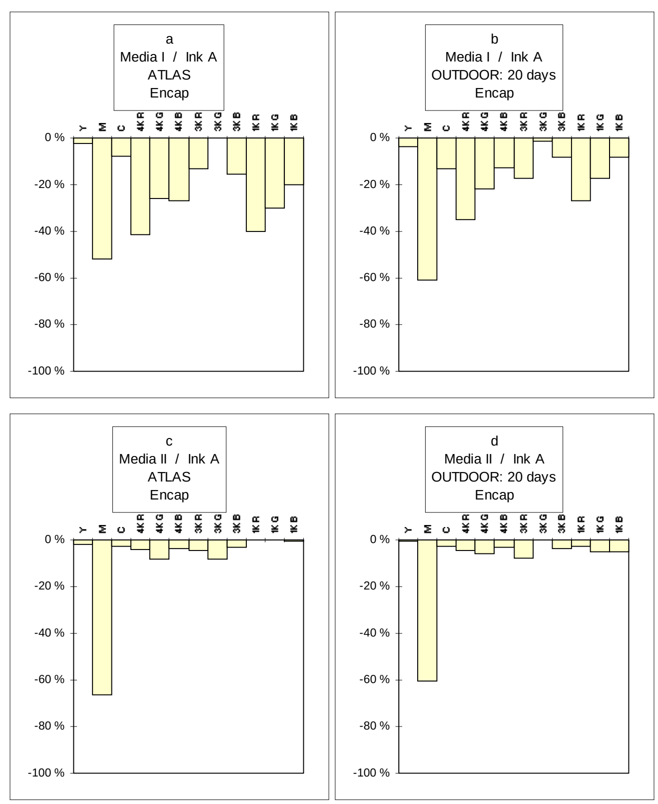


*Figure 7: Accelerated and real time fading for one ink on two different media and non-UV protective laminate*

The same ink and media combinations were investigated again but with a different, UV-protective laminate (Ilfoguard Coldlam UV). Figure 8a and 8c show the accelerated fading data, figure 8b and 8d the actual outdoor exposures. The prediction of the laboratory test for the actual outdoor exposure is again excellent.

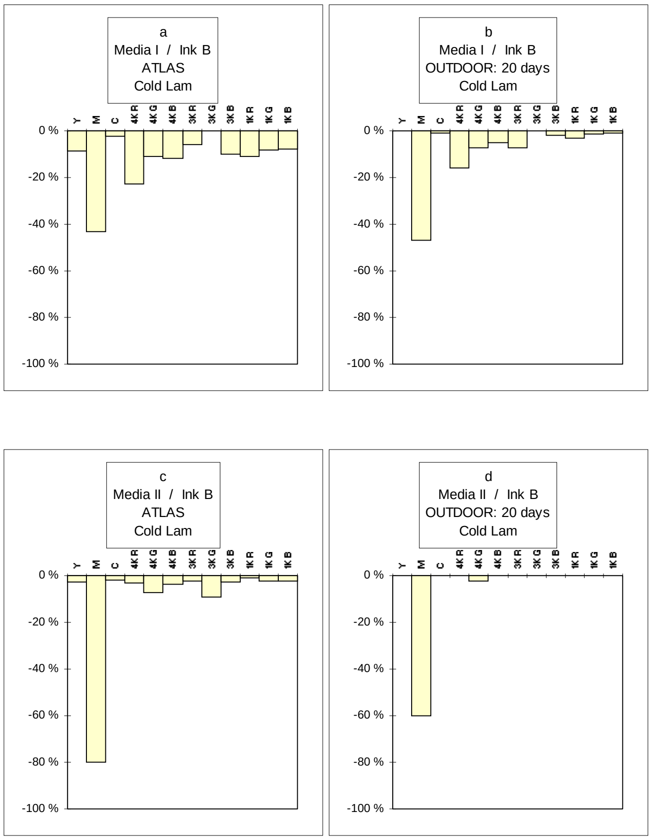


*Figure 8: Accelerated and real time fading for one ink on two different media and with-UV protective laminate*

The comparison between figure 7a, 7b and figure 8a, 8b as well as figure 7c, 7d and figure 8c, 8d shows the influence of a UV protective laminate compared to a solely encapsulating laminate. The main difference between figure 7 and figure 8 is the spectral composition of light hitting the sample. On media I (a,b) the UV protection improves the light stability and density losses are smaller for most colours. Magenta is the only colorant that is hardly protected by cutting UV light out, because this is a colorant that is highly sensitive to visible light as well. Media II (c,d) has by itself a UV protective effect and the UV shielding of the laminate does not contribute as much.

The comparison between media I and II shows one additional effect that may happen in fading. Whereas 1K black and cyan fading are reduced going from media I to II, magenta loses more density. The components that stabilize one type of colorant may well de-stabilise others.

Figure 9a - 9d represent the data of media I and media II with a different ink B, both laminated with an Encap laminate. Figure 9a and 9c are the accelerated fading samples, figure 9b and 9d the outdoor tests. The laboratory test correspond again well with the actual outdoor tests. The very strong stabilising effect of media II on B is clearly visible on all colours. This is an another example of the degrading or protective properties form the film forming matrix

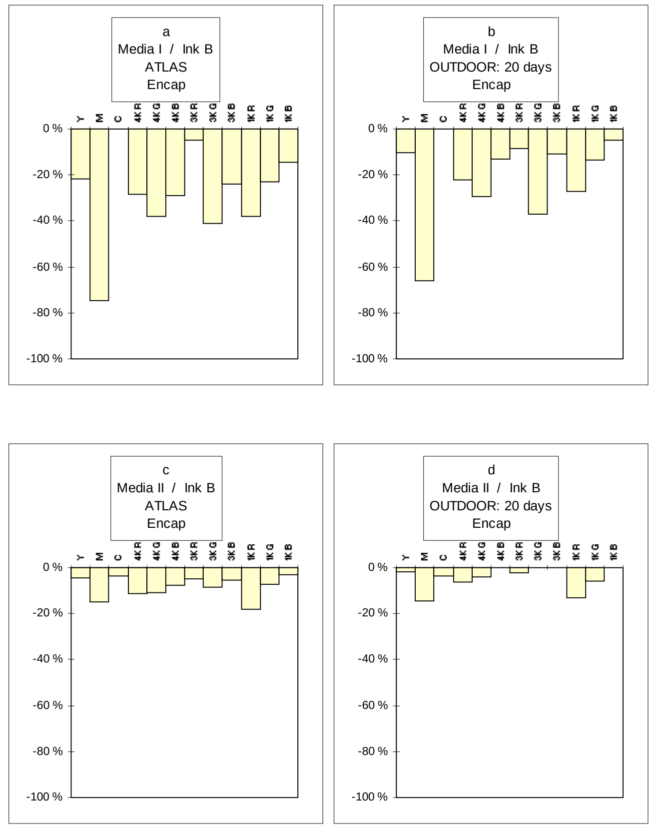


*Figure 9: Accelerated and real-time light fading, one ink (different from figure 7 and 8) on two different media with non-UV protective laminate*

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## References

1. H. Wilhelm, The Permanence and Care of Colour Photographs, Preservation Publishing Company, 1993