The Influence of Media on the Light Fastness of Ink Jet Prints

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Abstract

Ink jet printing has become one of the major imaging technologies used in digital printing applications. The versatility of ink jet has led to an ever increasing number of applications for this technology. In addition to the well established SOHO or desktop market segment, ink jet has now diversified into the business/network, wide format, photo realistic and textile printing applications. These require better image durability in order to provide a print performance as good as existing photographic, lithographic, screen or offset printing technologies. For many of these applications the print must be stable for many years for archiving or the preservation of an image exposed to the environment. The light stability of prints is of particular importance and the improvement of the photo stability of ink jet prints is an important goal.

The most important factors in determining the light fastness, of an ink jet print, are the colorant or chromophore, the ink formulation and the ink/media interactions[1]. The photo stability of pigments tends to be superior to that of dyes, however, recent developments in dye chemistry combined with the optimization of ink/media interactions, to protect the chromophore, have produced soluble colorants with light fastness acceptable for many ink jet applications.

There has been a rapid development of special media for ink jet applications and in particular for photo realistic and outdoor wide format printing. It has become increasingly clear that the actual environment of the colorant also plays a key role in determining the photo stability of the ink jet print.

Introduction

Most current colour ink jet systems are based on aqueous ink formulations containing water soluble dyes. Black pigment inks are used in desktop applications and together with coloured pigment formulations have been introduced for applications requiring high light fastness, e. g. wide format printing. The oil based pigment ink formulations used in the Xaar print head were chosen for both their superior light fastness, compared to most dye based inks, and their print performance in certain areas, for example, the absence of cockle and rapid drytimes[2].

For many of the newer ink jet applications special media is required and this has led to developments in matched ink and media systems in order to obtain the optimum print performance.

This influence of the colorant/ ink formulation together with the chemicals and environment of the media surface will be discussed in the present paper. Besides the inherent photo stability of the colorant itself there are a wide number of factors which can further influence the light fastness performance of a print. These can include the temperature and humidity to which the printed image is exposed, the pH, the chemical composition of the media surface, diffusion/ migration of the colorant into the coating layers and the chemical and physical form of the colorant and ink system.

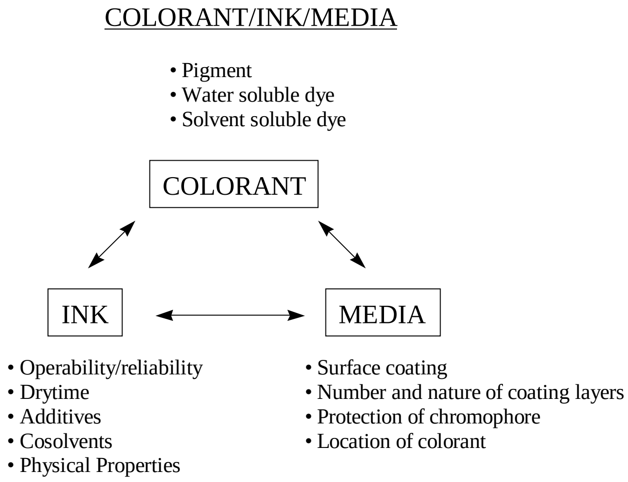


Figure 1. Interactions which influence the light fastness

The key interactions are illustrated in figure 1.

The selection of the colorant/ink system and the media must take account of the overall ink jet system in order to provide the print performance required by the end user.

Light Fastness Test Methods

There are several approaches for determining the light fastness of images. The simplest and most realistic would be to expose the print sample to actual daylight. This would indicate true lifetime of the printed image under real time conditions. However, the many problems associated with such methods and the time taken to achieve results are well known. The alternative, accelerated exposure testing methods using xenon arc lamps have become well established allowing reproducible results to be produced in short time scales. Various standard procedures are available for accelerated light fastness testing which detail sample type and preparation, equipment, exposure conditions and measurement.

In this study the test equipment was the Xenotest 150 (Hanau) using a regulated relative humidity of 40%.

Results are quoted as colour difference (ΔE) units in CIEL*a*b* colour space. Measurements were made using an X-Rite SP78 Spectrophotometer using illuminant D65 and a 2 degree observer for the special media prints and D65 illuminant and 10 degree observer for textile print exposures (where $\Delta E = [\,(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$).

Textile prints were assessed by the Blue Wool Scale(BWS)(ISO Methods :Light Test Method B2) and by ΔE (50 hours exposure) measurements.

A tentative relationship has been established between the BWS scale and ΔE (after 50 hours exposure) in the blue wool scale area of 1 to 4 in the current work. (figure 2).

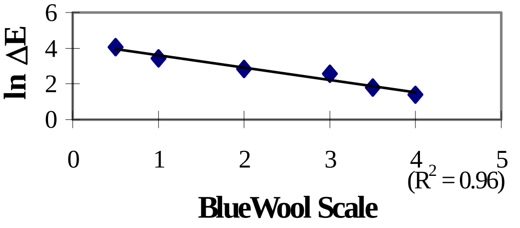


Figure 2. Plot Relating the ΔE scale to the Textile Blue Wool Scale

Influence of Colorants on Light Fastness

The selection of colorants for ink jet applications depends on the print performance requirements demanded by the specific end use that the print will be subjected. Before considering the actual light fastness mechanisms and the major factors that can influence these mechanisms it is opportune to more fully understand the chemistry of the colorants found in current ink jet applications.

Black

Most black dyes used in ink jet are based on the azo chromophore. These will usually be large aromatic structures containing disazo, trisazo or even tetraazo chromophoric groups in order to absorb most of the light in the visible region of the spectrum. They generally have very good light fastness and are widely used in many ink jet print applications.

For pigment ink formulations, carbon black is commonly used. These inks provide prints with high optical density and good image durability and have consequently found application in desk top applications.

There are some metallised azo black dyes containing copper, chromium or cobalt. These can either be aqueous or solvent soluble dyes. Due to the protection of the chromophore, by the metal cations, these dyes do tend to have better photo stability performance.

Yellow

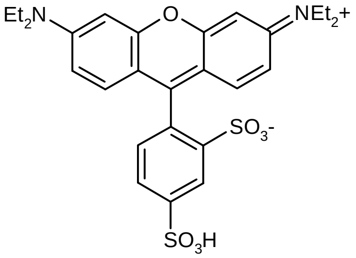
In the dye area the chemistry is mainly based on azo chromophores. The azopyridones and azopyrazolones (C. I. Acid Yellow 23) exist exclusively in the hydrazo tautomeric form, due to the presence of an internal hydrogen bond, however, this grouping does make them more susceptible to photo decomposition.

Yellow pigments for ink jet applications[2] include the monoazo acetoacetarylamides and isoindolines, both these chromophore types have high light fastness.

Magenta

Magenta dyes usually have the lowest light fastness in ink jet and, indeed, in most other colour applications. Most of the work described in this paper refers to studies on magenta colorant systems.

One of the most commonly used magenta dyes for desktop ink jet printers, is C. I. Acid Red 52 (1) which comprises of a xanthene chromophore. This is a fluorescent dye with very high chroma but poor image durability. This has now largely been replaced in many ink jet applications, which demand greater photo stability for the printed image.



Acid Red 52 (1)

Other magenta dyes are based on azo chromophores. The light fastness differs markedly depending on the structure and the substituents attached to the chromophore. The two most commonly used azo magentas, are those based on H-acid (figure 3)and those based on Gamma acid (2). The H-acid dyes are bright but have moderate light fastness due to the existence of the hydrazo tautomeric form.

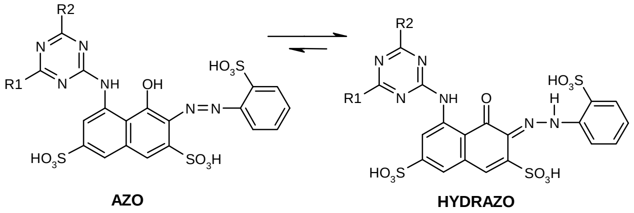
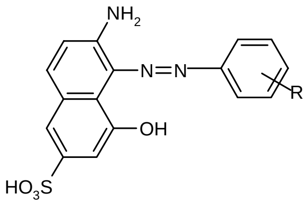


Figure 3. Tautomeric forms of an H-acid Magenta Dye

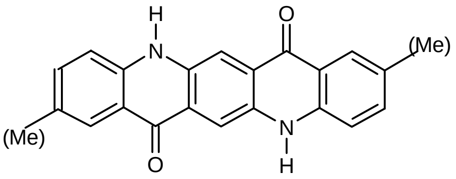


Gamma Acid Magenta (2)

The magenta dyes based on Gamma acid exist only in the azo form. As a result, these dyes have higher light fastness and have found use in photographic applications. Gamma acid based magentas have lower chroma than the H-acid magentas, probably due to the aggregation of these dyes on the media surface.

Quinacridone (3) or dimethylquinacridone are the most commonly used magenta pigments, for ink jet applications.

This chromphore exhibits very high light fastness.



γ Quinacridone (3)

Cyan

Most of the cyan colorants, both dyes and pigments, used in ink jet printing are based on the copper phthalocyanine chromophore which has excellent photo stability on the majority of substrates. The only other cyans used are based on the triphenylmethane structures, such as C. I. Acid Blue 9, this chromophore has extremely poor photo stability performance.

The Mechanism of Photo Fading of Colorants

Most colorants undergo oxidative fading in the presence of light, moisture and oxygen. In certain specific cases reductive fading can occur, but this mechanism is less common.

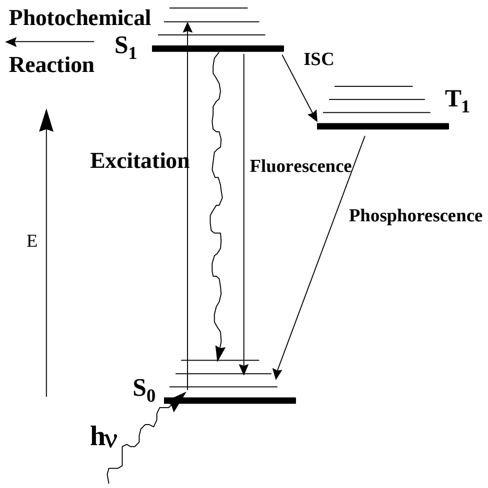


Figure 4. Chromophore excitation by a photon of light

On absorbing a photon, the dye is excited to the first or higher excited singlet state as shown in schematic form in Figure 4. This can then return to the ground state either directly resulting in fluorescence or by “inter system crossing” (ISC) to the triplet state. Alternatively the colorant can undergo a photo chemical reaction in this highly reactive excited state. Dyes with long lived excited singlet states tend to undergo photo degradation quite rapidly. By reducing the lifetime of the dye, in the excited singlet state, then the photo stability can be increased. Relaxation to the ground state can occur by several routes shown schematically in figure 4.

Other factors which are important include the light source, the absorption characteristics of the dye and the lifetime in the S_1 and T_1 states.

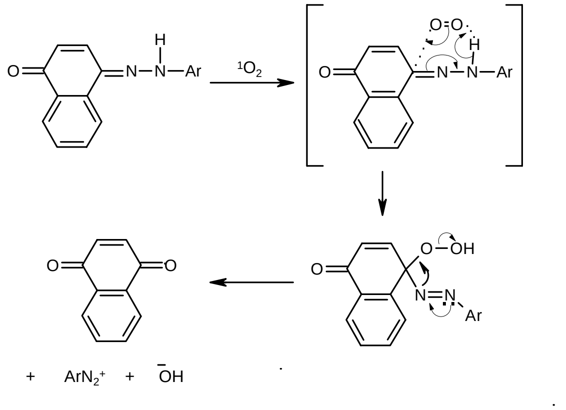


Figure 5. The oxidative destruction of an azo chromophore

The oxidation of azo dyes has been studied by various researchers and the mechanism of the decomposition has been investigated[3, 4]. For example, the proposed mechanism for the photo decomposition of an azo naphthol dye, which largely exists in the more stable hydrazo tautomer, is illustrated in figure 5.

The mechanism involves the attack of singlet oxygen on the azo or the hydrazo tautomer to produce a peroxide which rapidly decomposes producing the naphthoquinone.

Reductive mechanisms are also possible on protein substrates, such as gelatin, silk or wool.

Figure 6 contrasts the kinetics of photo decomposition for a commonly used aqueous ink jet dye set. This illustrates some of the comments made in the colorant section that the cyan is the most stable chromophore, whereas the magenta is the least stable.

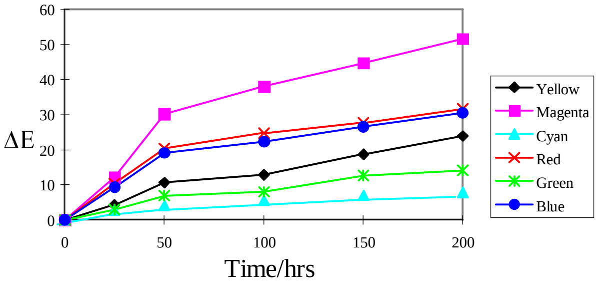


Figure 6. Plot of the Rates of Fade of Primary and Secondary Colours

For secondary colours, the red and blue have almost identical fading rates whereas the green has a rate of fade close to that of the cyan. Ideally all primary, secondary and tertiary dye combinations should fade at the same rate producing an "on tone " fade. This is difficult to achieve and for certain dye mixtures there can be further problems associated with the influence of one dye on another. This may involve the accelerated photo oxidation of the least stable chromophore in the mixture. This can be a significant problem in photo realistic ink jet, where similar photo fading of all colorants is required.

In the example shown in figure 6 the print would go greener, on prolonged exposure to light, due to the disappearance of the magenta dye prior to the yellow with the cyan being the last remaining colour.

Influence of Media Properties on Light Fastness

As discussed in the previous section colorants applied to protein structures tend to undergo reductive fading whereas colorants on cellulosic, polyhydroxy coated or polyester susbtrates tend to undergo oxidative fading[3].

However, the actual environment of the colorant in both the ink formulation and the media can also have very significant influence on the overall print image photo stability performance.

Some of these important factors, such as the pH of the media, the chemical composition of the media surface, the location of the colorant within the media, influence of formulation additives, the physical form of the colorant will be briefly discussed in the remainder of the paper.

Media pH

The inorganic oxides, such as silica and titanium dioxide, tend to produce acidic surface layers whereas the amphoteric effect of alumina produces a more neutral pH. Use of the filler $CaCO_3$ produces a basic surface.

Acidic pH values can favour the hydrazo form of certain yellow, magenta or black azo dyes. The azo form, favoured at higher pH, does have a better light fastness.

The acidic pH can also affect dye solubility leading to crystallisation or aggregation on the paper surface.

Physical Form of the Dye

When a dye crystallises on the surface of the media the colorant is protected by the aggregation of the molecules into nanocrystallites with the molecules at the surface protecting those trapped within the crystal. This can be observed for dyes with aqueous solubilities which are pH dependent. The carboxy functionalised ink jet dyes[5] behave in this way with the dyes aggregating in an extensive hydrogen bonded network forming nanocrystals on the media surface.

Additives

The use of ink formulation additives can influence the photo stability, they are usually aqueous soluble chemicals used at low concentrations in the ink to protect the chromophore. Dependent on the photo fading mechanism, oxidative or reductive, the addition of reducing agents or antioxidants could be made.

These additives could also be used in the media surface coatings, albeit at higher concentrations.

Ink formulation additives such as u. v. absorbers, singlet oxygen quenchers, radical quenchers etc, were not very effective in reducing the photo fading with our current studies.

Influence of Surface Coatings

There is now a vast range of media available for ink jet printing. In addition to the many plain papers there is an increasing number of special or coated media containing single or multiple layers to provide the optimum image properties. The surface is often quite porous to aqueous inks allowing the rapid penetration of the ink vehicle into the image receiving layer. In addition, these ink absorbent coatings may be capable of fixing dyes and providing protection from photo fading. The most commonly used polymeric systems include methylcellulose, carboxymethyl cellulose, polyvinylalcohol, polyacrylates and gelatin. The majority of these polymer systems are very good at absorbing the ink vehicle and have limited effect on the photo stability of the image.

Coating layers containing PVP and polycationic systems can significantly reduce the photo stability of dyes. For magenta dyes, most cationic coatings cause a bathochromic shift in the λ_{max} leading to bluer, duller shades. Light fastness is often lowered in the presence of organic cations whereas for inorganic cations, particularly the transition metal ions, an increase in photo stability can often be achieved. However, the resultant printed image has a much reduced chroma.

Influence of Metal Cations

Metal complex dyes are often the most stable to light. Copper phthalocyanine and other metal phthalocyanine dyes are among the most stable dye chromophores. Use of metal cations to protect chromophores does result in a significant increase in light fastness, however, the general downside is the dulling of coloured chromophores.

Figure 7 indicates how the Cu^{2+} cation coordinates the azo group in a dye forming a chelate complex.

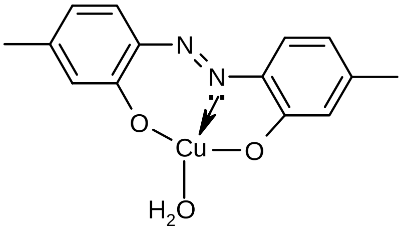


Figure 7. Coordination of Cu^{2+} to an Azo dye

This coordination mechanism increases the light fastness quite significantly[3] by reducing the electron density in the chromophore, making it less susceptible to oxidation, and also by protection of the azo linkage.

Many black dyes uses in ink jet are metal complexes containing Cu^{2+}, Cr^{3+} or Co^{3+}.

By coating the surface of the media with transition metal cations, the photo stability of dyes can be increased. The resultant transition metal complexes however, often cause slight discoloration of the media with consequent dulling of the image.

Location of the Colorant

Figure 8 illustrates how a dye penetrates into a photo ink jet paper. The porous surface layer can help to protect the chromphore from light degradation. In addition the nature of the image receiving layer, in which the colorant resides, can also dramatically influence the photo stability performance. Gelatin and poly hydroxy polymers are usually the best for this chromophore protection.

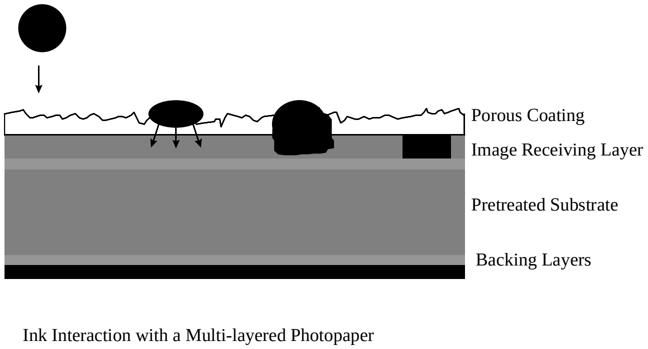


Figure 8. Absorption of an Aqueous Ink into a Photo Paper

The influence of dye penetration into a glossy film is illustrated in figure 9. The light fastness is improved by increasing the diffusion of the dye into the surface coating layers on a substrate. This is most likely due to the additional protection provided by the outer coating layers.

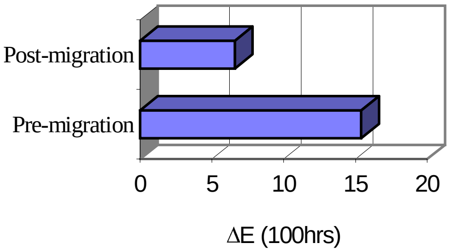


Figure 9. Influence of Diffusion on Light Fastness for a Glossy Film

Lamination

By overcoating (laminating) a print with a polymeric coating, which may contain a uv absorber, the light fastness of the image can also improved, due to the inaccessibilty of the colorant to moisture and O_2. Studies of dyes at increased temperatures and humidities indicate that photo degradation increases quite markedly and the use of lamination obviously provides protection.

Influence of the Ink

There are many complexities involved in the design of ink jet ink formulations. There are several factors, in the ink formulation, which influence the photo stability of the colorant. Inks containing lower dye concentrations produce pale images which can fade rapidly. For photo realistic applications, where low concentration cyan and magenta inks are included in the ink set, the photo fading of the pale magenta shade can be particularly poor. This has increased the requirement for a much better light fast magenta for such applications. The volatility of the cosolvents and their ability to penetrate, or to facilitate the dye diffusion into the media, are also important. The less volatile glycols such as tetraethyleneglycol and polyethyleneglycols, etc do evaporate more slowly and so remain with the colorant in the media for prolonged periods. These retain high concentrations of moisture and O_2 close to the dyes, accelerating photo oxidation leading to a reduction in photo stability

Light Fastness of Colorants on Textiles

The influence of a range of different media including textiles has also been studied The protein substrates, such as silk and gelatin coated photo papers, tend to have good light fastness for most azo based magenta dyes.

The cellulosic fibres, such as cotton and viscose, also display good photo stability. For example, with textile ink jet printing a magenta reactive dye will typically produce a light fastness of 4 on the textile blue wool scale due to the reactive dye forming a chemically covalent bond with the hydroxyl group in the cellulose fibre.

Disperse dyes on polyester also have good lightfastness due to the protection of the chromophores trapped within the fibre.

Conclusions

Besides the inherent photo stability stemming from the chemical nature of the colorant, the environment of the colorant has a strong influence on the stability of the chromophore to light. There are many factors within this environment which influence the photo stability. By maximizing the dye/media interactions and careful selection of the chemical composition of the surface coatings, the light fastness of the dye can be significantly enhanced. There is still room for further improvement of both the chromophore structures and the media chemistry. By careful selection of the dye/ink and media systems and optimizing their performance in ink jet applications, ink systems, containing dyes, can be developed to provide the performance required for many ink jet applications.

References

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Biography

Aidan Lavery received his BSc and PhD in Chemistry from Queen's University Belfast in 1980 and 1984, respectively. Dr. Lavery went to Edinburgh University in 1984 to carry out postdoctoral research. He then joined Huddersfield University as a lecturer in Chemistry in 1985. He joined ICI/Zeneca in 1988 and for the last five years has worked on ink jet systems. He is group leader for the Ink Jet Physical Science Group with interests in ink formulations and ink-media interactions.

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