

Color-Media Interactions in Ink Jet Printing

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Abstract

The influence of the recording medium on performance has become increasingly important in ink jet printing as the technology diversifies into a wide range of specialised applications. For photorealistic printing the image quality needs to aspire to that produced by conventional photography. This will require improvements in both the media and the inks. The final colorant selection depends on specific colour requirements as well as the ink, the media and the printhead technology for each application.

The interaction of the ink with the substrate is key to producing high strength, well defined, durable images fit for each application. Colorants considered include acid dyes, direct dyes, reactive dyes, solvent soluble dyes and pigments. These colorants are either dissolved or dispersed in the ink and applied, to the substrate, by ink jet printing. The key interactions take place at the surface of the substrate and the nature of the bonding plays an important role in determining the print quality. This paper describes the colour-media interactions and includes molecular modelling studies which have been used to help identify the optimum systems for particular ink jet applications.

Introduction

Ink-jet printing has become the major printing technology in both the desktop and industrial applications.[1,2] The advent of digital colour printing has opened up many new application areas for ink jet including wide-format, graphic arts and textiles which, until recently, were the domain of the traditional print technologies. These will provide considerable opportunities in the consumables business particularly for the media and the ink.

As the industry moves towards these new ink jet markets then the media, whether it be coated paper, film or textile substrates, becomes an integral part of the technology and knowledge of the chemistry of the ink/colorants and the media becomes increasingly important.

The present paper will highlight the complex nature of the surface interactions which occur when a colorant is printed onto a substrate. The term media in this paper refers to plain and coated paper, film and textiles.

End User Requirements

Whatever the end user application similar selection criteria, for prioritising the performance characteristics, can be considered.

Image Quality	spectral, durability, resolution
Operability	priming, clogging, crusting, reliability
Flexibility	speed/drytime, substrate management, consumable costs.

The colorant impacts on each of these, however image quality is the area where the colorant has the greatest influence (see figure 1).

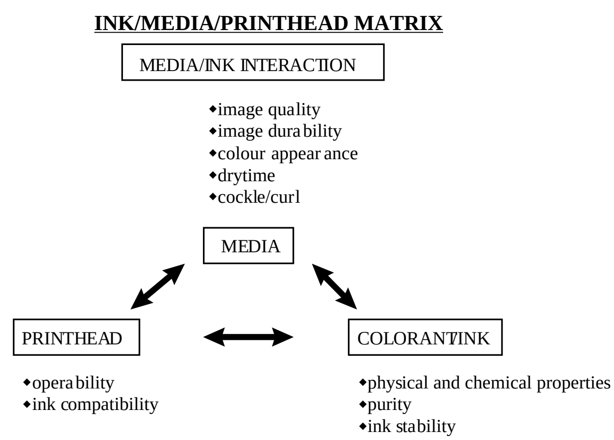


Figure 1. Interaction of the three key components involved in producing an ink-jet image.

Overall many of the factors are interrelated and the final colorant/ink selection must take account of the whole package in order to provide the print performance required for the end user application.

Colorants in Ink Jet Printing

The classification of colorants (see Figure 2) has been defined, according to their end use by the colour index (CI)[3]. The essential differences between insoluble pigments and dyes has been detailed previously.[4,5] The chemical nature of the colorant largely determines the extent of the interaction with the media. Those commonly used in ink-jet are described and examples of some typical yellow and cyan dye structures are given see **(1)**, **(2)** and Figure 3.

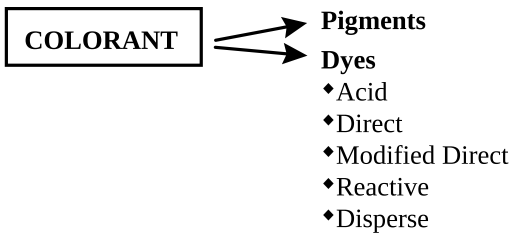
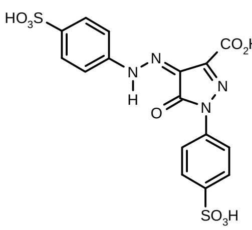


Figure 2. Colorants used in ink jet printing

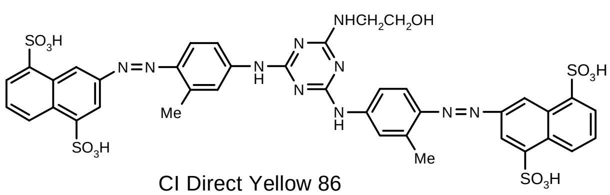
Acid Dyes These are low molecular weight anionic dyes which are relatively small in size. They have high aqueous solubility and are used for dyeing nylon and protein (wool and silk) fibres. They are also used in colour ink-jet printers due to their very high image intensity or chroma. The dyes diffuse readily through the media and have a low affinity for the substrate. Their poor image durability (wet-fastness and light fastness) has led to the replacement of these dyes for most new ink jet applications. Photorealistic, wide-format and other end user applications now demand a much higher performance from the colorants.



CI Acid Yellow 23

(1)

Direct Dyes These have higher molecular weights and are much larger in size than the acid dyes increasing their affinity for cellulosic media. Direct dyes are generally quite soluble in water and are characterised by large planar aromatic structures. These are not as bright as acid dyes but their wet-fastness and lightfastness is better.



(2)

Modified Direct Dyes These have been developed by Zeneca Specialist Colours to provide better image durability in ink jet printing. The term "modified direct dyes" has been introduced to describe more recent dye developments where the dye structures have added functionality to enhance the interaction with the media. The generation 1, 2 and 3 dye structures, shown in Figure 3, illustrate some of the structural modifications included to enhance the performance of these dyes in ink jet printing. For the generation 2 dyes the sulphonic acid groups, present in generation 1, have largely been replaced by carboxylic acids. These "carboxy dyes" have good aqueous solubility at high pH, however on lowering the pH, the solubility is greatly reduced leading to precipitation of the colorant on the media surface. For generation 3 dyes, the chromophores have additional functionality which further enhances the affinity of these dye molecules for the media particularly for cellulosic substrates. These dye molecules produce instant wet-fast prints when printed onto most paper types.

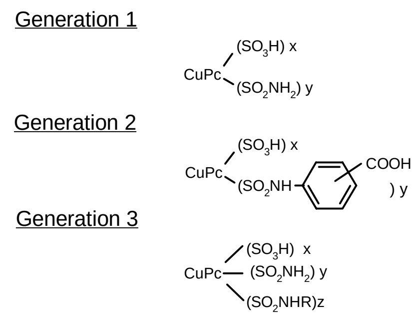


Figure 3. Structurally Modified Direct dyes for ink jet

Fibre Reactive Dyes These are high chroma, water soluble colorants, containing a reactive group, for printing onto cellulosic and protein substrates. There are many reactive groups but the monochlorotriazine, used in Zeneca's dye range, gives reliable performance in textiles ink jet with a wide range of printheads. The major advantage of using these colorants is that they form a covalent link with the fibre (see Figure 4). This produces a bright durable colour print on textiles. Due to the high temperature and pH required to fix the dye this interaction cannot be carried out on other media such as paper or film.

Disperse Dyes These are virtually insoluble in water but are solvent soluble. The dyes are applied as finely dispersed aqueous inks to the media. They have excellent chroma, and good image durability. They are used for hydrophobic substrates such as polyester.

Other Dyes Food dyes and cationic paper dyes(Basic and Cationic direct dyes) can also be considered however the Basic dyes have poor light fastness and cationic dyes would require the inks to be formulated at acidic pHs.

Pigments These are insoluble colorants which must be applied as fine particulate dispersions to the media. They have very good image durability but have no affinity for the substrates to which they are applied. This leads to rub fastness problems and also smearing of the print with highlighter pens. A high optical density black is obtained on plain paper, however the shade gamut and chroma of the coloured pigments has limited their use compared to dye based colorants.[6]

Colour-Media Interactions

The rate of adsorption of a dye onto the surface of a substrate depends on the nature of the interaction between the two.[7] For colorants with no affinity for the substrate eg pigments (or disperse dyes on cellulose) then the ink and the binder (usually required for colorants with no affinity for a substrate) play the key role. Most substrates have relatively complex chemical structures with multiple sites for binding dyes. Molecular modelling has been used to provide an indication of the likely binding energies of the dyes with cellulosic substrates such as cotton and plain papers. Metropolis Monte Carlo methods have been used to determine the surface interaction or binding energy for dyes to cellulose.[8]

A model for a cellulose surface was generated from crystallographic data and the binding energies determined by force field calculations summing the contributions from hydrogen bonding, electrostatics and Van der Waals interactions. Table 1 shows the binding energies for a series of black and yellow anionic dyes interacting with cellulose. By modifying the dye structures, to enhance the binding energy, more durable prints result with better image quality.

Table 1. Binding energies for the interaction of dyes with cellulose

Dye	Binding Energy (k cal mol^{-1})
Generation 1 Black	-42
Generation 2 Black	-56.4
Generation 3 Black	-98.4
Acid Yellow 23	-43
Direct Yellow 132	-58.8

There are a number of factors to consider when a colorant interacts with a substrate. The colorants consist of hydrated anionic dyes and this hydration sphere must dissociate for the colorant to interact effectively with the substrate. For the dye to be attracted to the substrate the dye--substrate combination must have a lower energy than the combination of the hydrated dye and the hydrated substrate. Hydrophobic substrates, such as polyester, do not interact with the water soluble colorants and so disperse dyes are used. Other important factors include:- (i) the printhead which influences the ink concentration (drop volume) and the frequency of drop formation and (ii) the ink. The latter will influence the rate of ink absorption into the substrate and the rate of evaporation of the ink vehicle.

The modes of interaction, between colorant and media, are reviewed in order of decreasing strength of interaction.

Covalent Bonding This is the strongest interaction which can occur and results from a chemical reaction between the colorant and the substrate. The electrophilic reactive group on the dye reacts with a nucleophilic group (a primary hydroxyl group on the cotton) producing an irreversible chemical reaction. This produces a print with excellent fastness properties.

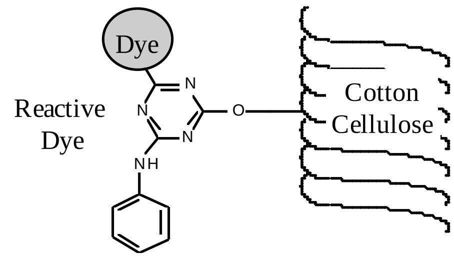


Figure 4. A covalently bound fibre reactive dye

Electrostatic or Ionic Interactions (coulombic attraction) Anionic dyes contain water solubilising groups such as, SO_3, COO^-, PO_3^{2-} and these are attracted by cationic groups on the media eg Ti^{4+}, Al^{3+}, Ca^{2+} , NR_4^+ producing a strong interaction and effectively immobilising the dye molecules giving excellent image quality.

π...π Interactions These are important in dye...dye interactions and can lead to dye aggregation or crystallisation. These are relatively strong interactions and may occur for media containing aromatic groups capable of interaction with the colorants. Chromophores such as the phthalocyanines aggregate using such interactions.

Hydrogen Bonding This is a fairly weak interaction however, for cellulosic substrates this is often the most important interaction between colorant and media. For a large dye molecule there may be a large number of sites for these interactions to occur increasing the strength of the binding. In addition there may be a number of T- bonding interactions involving the -OH of the cellulose interacting with the π–cloud of an aromatic group on the colorant.[9]

Hydrophobic Interactions This attraction occurs for solvent soluble dye systems which contain hydrophobic groups such as alkyl chains. These interact with similar hydrophobic groups on the substrate and this is quite favourable particu-larly when the colorant is applied from an aqueous phase. The interaction consists of a combination of Hydrogen bonding and Van der Waals interactions.

Dipole-Dipole Interactions These are relatively weak and result from the induced polarity in the interacting groups.

Van der Waals Forces These tend to be quite weak at long range but become stronger when the interacting groups are brought close together. A weak repulsion occurs between cellulosic substrates and anionic dyes when they are far apart however, as the water soluble dyes are absorbed then the interaction between colorant and media becomes quite strong. This is observed for most of the dyes and is also important in preparing aqueous dispersions of insoluble colorants.

Interaction with Plain Paper

All of these modes of interaction are present in textile ink jet however, for plain papers hydrogen bonding and Van der Waals are the key interactions whereas for coated papers and film ionic or coulombic forces are also important. Plain and modified papers consist of mainly cellulose and this is what the colorant interacts with when printed onto the paper surface.[10] For these papers the furnish as well as the internal and surface sizing play an important role in determining the print properties. For these papers the capilliary absorption of the aqueous inks influences how rapidly the ink diffuses into the substrate.

It is possible to design coated media to maximise the binding energy derived from the non-covalent interactions.

Interaction of the Colorant with Coated Media

There has been considerable growth in the development of coated media particularly for colour ink jet printing. This is a consequence of the increased demands placed on colour printing particularly in the photorealistic and wide-format application areas. A wide range of coated paper, film and photomedia is now available for ink jet and the choice of the media is key to achieving optimum performance. The coating formulations are a complex mixture of binders (polymers), pigments, fixing agents (cationic reagents), optical brighteners etc. The selection of the components both the coating and ink formulation has a significant influence on the image quality, fastness properties and the rate of ink absorption The ink vehicle must be rapidly absorbed by the media or a suitable polymeric coating to give a fast drytime. The diffusion of the colorant into the media must also be carefully controlled to provide the required image quality. The ink receiver layer must also retain its original surface characteristics such as gloss and avoid distortion or cracking of the coating. Dyes have greater versatility since their chemistry can be modified to match that of the media coating.

Coated media can contain inorganic oxides such as alumina, silica, talc, clay, titanium dioxide, calcium carbonate etc and also polymers such as polyvinyl-pyrrolidone (PVP), polyvinylalcohol (PVA), gelatin, carboxymethylcellulose and polyvinylacetate. The nature of the coating largely determines the image properties of the print. The interaction of the ink with plain paper, coated paper and photopaper is contrasted in Figure 5. For plain paper the ink is absorbed by the cellulose and spreads out in all directions both on and beneath the paper surface.

For anionic dyes the colour-media interactions are relatively weak and are mainly due to hydrogen bonding and Van der Waals interactions. Coated papers however, interact much more effectively with dyes fixing the colorant in the vicinity of where it was printed.[11] The increased interaction is largely due to the presence of electrostatic interactions between the anionic dyes and the inorganic oxide. This interaction greatly increases the binding energies for the dyes and leads to high strength, high chroma prints with no colour to colour bleed, excellent dot definition and perfect wet-fastness in most cases.

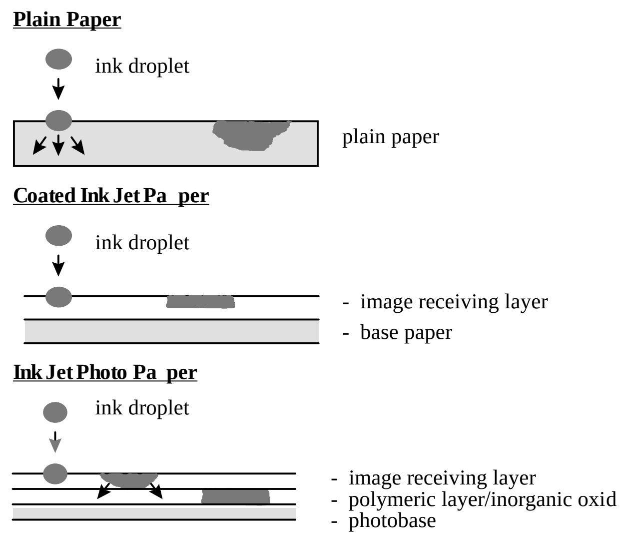


Figure 5. Ink absorption by plain and coated media.

Photomedia display similar properties however since the colorant diffuses further into the coating, the photostability or light fastness is enhanced due to the dye being protected by the outer surface coating (figure 5).

Influence of the Ink

The ink properties have a considerable influence on performance. This is illustrated in Figure 5. A penetrating ink can be absorbed by a plain paper within milliseconds with most of the aqueous ink vehicle being absorbed by the cellulose. If the internal sizing is low, or the paper is unable to cope with the volume of ink, then strike-through can occur.

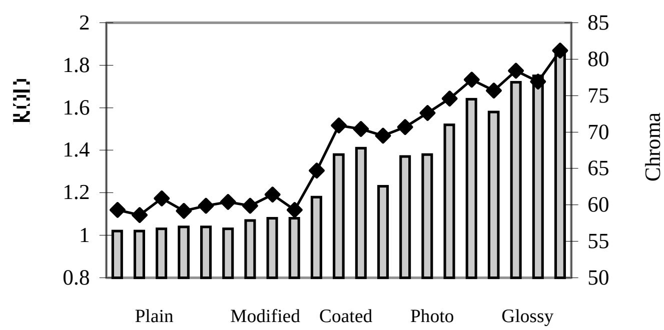


Figure 6. Influence of the media type on optical density. The Chroma is the line plot and ROD the bar chart.

Non-penetrating inks are absorbed more slowly, taking 10-30 seconds to be absorbed into the paper. This produces high optical density prints with no strike-through. Future printers will require rapidly penetrating inks to give fast drytimes and faster print speeds. This will almost certainly require the media to be able to cope more effectively with the absorption of the ink vehicle.

Image Properties

When the dye...dye interactions compete with the dye...substrate interactions, then the colorant can aggregate or crystallise on the paper surface leading to a loss in optical density. Although this effect can enhance the image durability it normally results in unsatisfactory colour rendition. This can be observed as bronzing, for certain black inks and as reduced chroma or dulling for coloured inks. These problems can be overcome through careful selection of the ink formulation and also by increasing the attraction of the colorant for the paper. The optimum performance is achieved by maximising the colour-media interactions. This is demonstrated for a magenta, ink printed onto a range of media types, in Figure 6. Printing onto glossy film enhances the ROD and chroma of the image quite significantly. The colour map, Figure 7, illustrates how the increased chroma of the dyes on glossy film also enhances the colour gamut.

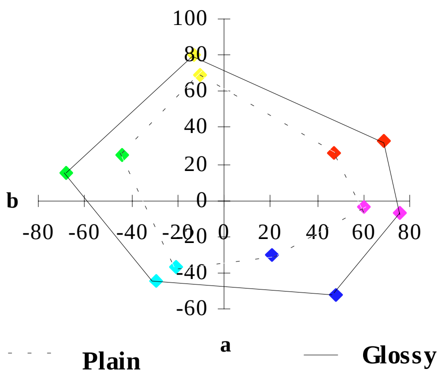


Figure 7. Colour gamut for Modified Direct Dye set.

Light Fastness

Ideally the colour should be fixed close to the surface with the ink vehicle being rapidly absorbed. Cationic reagents have been found to give the best results with anionic colorants. While the image quality is greatly enhanced the photostability can suffer. This can be a problem where the colorant is fixed at the surface of the substrate since the chromophore is directly exposed to uv light leading to the photodecomposition of the dye. The influence of substrate on light fastness is illustrated in Figure 8. Light fastness has been measured by ΔE by fading a magenta dye in a weatherometer for 100hrs. ΔE is a measure of the colour difference between the faded and unfaded prints. The glossy films and coated papers have poor light fastness whereas for the ink-jet photopapers the light fastness of the dyes is frequently enhanced most likely due to the protection of the surface coating or polymer layer.

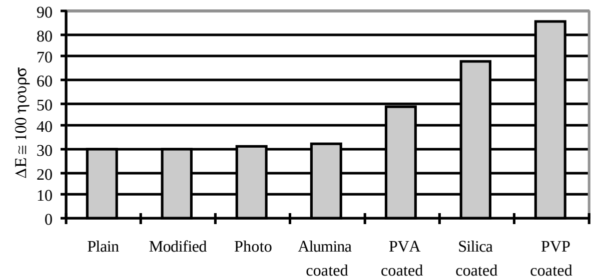


Figure 8. Influence of media on light fastness.

Interaction of Colorants with Textile Substrates

Textile ink jet printing requires an additional fixation step compared to other ink jet applications. This involves steam fixation of the dye to the fibre at high temperature(100-180°C). Any unfixed dye is removed by a separate washing process.[12,13] This requires the correct selection of colorant for the textile substrate to be printed. In addition, a pretreatment is required to apply the reagents required to fix the colorant to the fibre.[14] This is a consequence of the printhead design which limits the components which can be added to the ink. The development of the ink formulation is critical as the cosolvents and additives must be compatible with the colorant and the printhead and must not inhibit dye fixation to the fibre. Table 2 summarises the colorant requirements for textile ink jet printing. A pigment/binder system would appear to offer a universal solution, however these systems tend not to be favoured due to the affect on fibre "handle" caused by the presence of the polymeric resin used to fix the pigment. This is in addition to problems associated with formulating an ink containing a stable fine particulate dispersion which can be problematic with certain head technologies.[14]

Table 2. Colorant selection for textile substrates and the mode of interaction with the fibre.

Colorant	Fibre	Colour-Media Interaction
Reactive dye	Cotton, silk and wool	Covalent
Acid dye	Silk, wool and polyamide (nylon)	Electrostatic, H bonding
Disperse dye	Polyester	Hydrophobic
Pigment	All fibres	None

To illustrate the interaction of the colorant with textiles the fixation of reactive dyes to cellulose polymers (merceried cotton) has been chosen. The mono-ochlorotriazine reactive group forms a covalent bond by reaction with a hydroxyl group on the cellulose. The reaction takes place with heat under alkaline conditions (see Figure 9).[14] It is important that the reaction conditions are controlled so that the dye reacts with cellulose rather than being hydrolysed by the alkali.

As the ink formulation generally contains cosolvents/ humectants, which also contain hydroxy groups, capable of preferentially reacting with the dye, considerable expertise is required to produce a stable ink formulation containing the reactive dye.[15]

The design of a method for uniformly coating (pre-treating) the textile substrate is important for the design of the total ink-jet system. The pre-treatment also requires the application of other chemicals (i.e. alkali, urea, sodium alginate thickeners) necessary to achieve the fixation of the reactive dye onto cotton. These cannot be included in the ink formulation as the physical properties of such an ink would make it unsuitable for firing in an ink jet printhead and so these must be applied in a separate stage. Each of the colorant/substrate combinations, Table 2, requires a different pre-treatment and ink formulation.

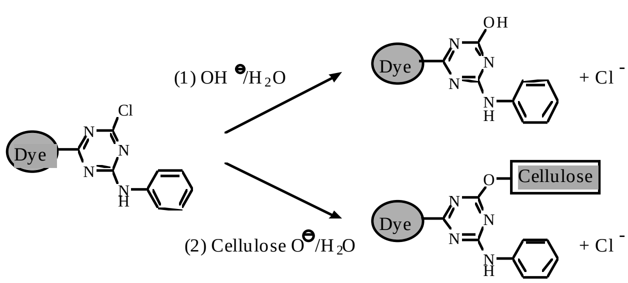


Figure 9. (1) Hydrolysis of a reactive dye. (2) Fixation to cellulose.

For cellulosic fibres the pre-treatment consists of a quaternary ammonium salt which can be used to bind the anionic reactive dyes containing sulphonic acid groups.[17] This electrostatic interaction effectively immobilises the dye on the surface of the cotton. On fixation in the steamer(102^{o}C) the dye becomes covalently bound to the fibre and this produces bright, durable, high quality prints equal to those produced by conventional printing technologies.

By designing the pretreatment chemistry, with the knowledge of the interaction between the dye and the fibre, considerable benefits in colour yield and print performance can be achieved.

Conclusions

By understanding the chemical nature of the colorants, used in ink jet, together with their modes of interaction/fixation to the media (paper, coated paper, films, textiles etc.), systems can be developed which can maximise the benefits of the colorants and at the same time improve the image quality and durability. The binding energy, for the colorant to the media, has a significant influence on the fastness properties of the prints. By carefully selecting the dyes and the chemical constituents in the media coating, a matched set can be found which will produce the highest quality images for specific ink jet applications.

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