Dye Recognition in Ink Jet Photopapers

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Abstract

A lot of research effort has gone into the design of inks and coatings for ink jet. Much of this has focused on producing digital photographs that have image properties close to those of silver halide. The most successful developments have involved the development of the ink and media in combination to produce a matched system.

In order to achieve AgX levels of performance an ideal environment must be created in the coating, such that the dye can be fixed and also protected from the environmental fading mechanisms. The design of dyes for specific environments was a key feature of textile dye development. By changing the pigments, binders and additives in the coating, the image stability for dye-based ink systems, can be greatly influenced.

Most of the water-based inks contain anionic dyes,[1-3] which are most effectively fixed by a highly cationic surface coating. In addition, further interactions can take place via hydrogen bonding, dipole/dipole, Van der Waals etc. By careful selection of the optimum environment for the dyes, the image properties can be significantly influenced.

The development of new dye structures and the optimisation of the media for these can produce a very durable image. Indeed there are some good examples, in the latest photoprinters, where the OEMs have achieved excellent image stability by developing the ink and photopaper in combination.[4]

Introduction

The photopaper development has been based on either the traditional resin coated photographic substrates, which contain a polyethylene barrier layer, or on paper glossy products where the coating is applied directly onto the rawbase paper.[5] For all these media types a rapid dry time and excellent image quality are essential features.

There is a large range of media available for digital imaging icluding glossy films, canvas, vinyl, textiles and also a wide range of coated and plain papers. The image properties depend primarily on the chromophore but the influence of the environment is also crucial. Dyes are coloured molecules which normally have an affinity for the substrates to which they are applied.[1,2] This substrate recognition, by a particular dye structure, provides a host/guest (dye/media) interaction which can encapsulate the dye into a more stable environment and significantly enhance the properties of the resulting image.

Table 1. Colourants for Ink Jet

Insoluble Colorants	Water soluble Dyes
Pigments	Acid
Surface Modified Pigments	Direct
	Modified Direct
	Photographic
	Hydrolysed Reactive

For a given ink system, dye or pigment based, the media can influence many of the image properties including colour density, brightness, hue, mottle, bleed and dry time. The receiver layers or surface coatings, applied to the substrate, play a very important role in determining the image properties and in particular the image durability. The chemistry of the coating can interact with the ink, when the image is displayed, exposing it to all the environmental fading mechanisms including light, ozone and humidity.[6-9] The image can also fade in the dark.

Influencing Factors on Photo Quality

The main factors, that influence the production of digital images, are illustrated in Fig. 1.

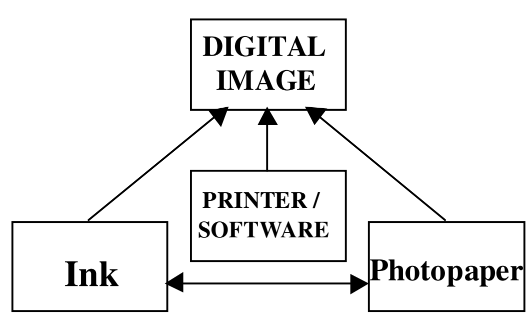


Figure 1. Producing a Digital Image by Ink Jet

The ink and media are the two components with the greatest influence on the image stability properties. The printer and printhead in combination with the colour management software also play an important role. The ink cosolvents i.e. water and glycols must be absorbed quickly into the coating.[3] The water evaporates fairly quickly after printing, depending on the nature of the coating, whereas the glycols tend to remain in the coating for longer. The presence of cosolvents in the coating can lead to problems with dye migration and bleed over time particullarly at high humididty. The coating itself influences the stability of the colourants by either fixing the dyes or by a physical interaction with pigments or dye aggregates. The environment provided by the coating can be oxidising or reducing and this influences the kinetics of dye degradation.

Matching Dyes to Media

The majority of printers contain dye based ink systems and these probably still account for greater than 80% of colourants used in the current printers. Pigment inks account for the remainder although these are probably on the increase.

Typical dye systems, used for ink jet,[3] are shown in table 2 below and the different types of bonding interaction are indicated. Generally the dyes need to penetrate into the substrate, to which they are applied, to derive the greatest protection from the substrate environment. When the dyes remain at the surface then they tend to more susceptible to the environmental fading mechanisms.

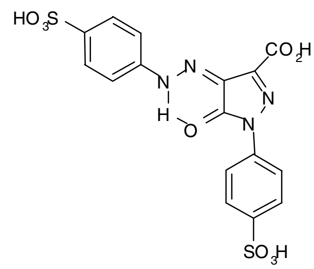
Table 2. Bonding Interactions of the Dyes with Substrates

Colorant	Application	Bonding Interaction(s)
Acid Dyes	Silk, Wool, Nylon, Ink Jet	Electrostatic, **H** bonding
Direct Modified Direct Dyes	Cotton, Ink Jet, Viscose, Paper, Leather	Electrostatic, **H** bonding Aggregation (π ... π)
Reactive Dyes	Cotton, cellulosic, Fibres	Covalent
Pigment	All fibres and Ink Jet	No interactions
Modified Pigments	Ink Jet	Electrostatic, **H** bonding

Acid Dyes

These were developed primarily for application to polyamide fibres under acidic conditions.[2] These dyes have been optimised for nylon, silk textiles and bind to the fibres mainly through electrostatic interactions. Within a polyamide environment these dyes are quite stable and provide bright durable colours. They have been used in ink jet printers due to their very bright colours and high aqueous solubility.

Gelatine (used in many of the swellable polymer coatings for photomedia) is derived from leather (collagen) and like wool and silk is based on a protein structure consisting of sequences of the amino acids Glycine-Proline-Hydroxyproline which are H-bonded in a helical structure. The anionic sulphonic acid groups, present in the Acid dyes (e.g. Acid yellow 23, Acid Blue 9 and Acid Red 52), interact with the protonated amine groups on the protein structure giving a strong electrostatic interaction.



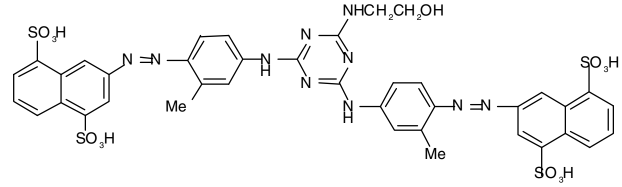
Acid Yellow 23

Dyeing is normally carried out at acidic pH where the amine functionality can be protonated providing a cationic charge to attract the dyes. Acid dyes also have a good affinity for gelatine. Since gelatine provides a reducing environment for dyes the resulting combination of acid dyes with gelatine gives a favourable dye/media interaction with good dye durability.

Acid dyes on other coatings, e.g. the microporous, where the dyes are relatively exposed to environmental fading mechanisms, tend to be quite unstable and have poor durability to light and other environmental influences.

Direct Dyes

Direct dyes were developed for application to cellulose substrates. Thus they are very substantive(have a high affinity) for cotton, viscose, and paper substrates. The high affinity is a result of H-bonding Van der Waals and dipole dipole interactions on the substrate surface and π…π interactions between the dye molecules forming dye aggregates within the substrate. Their high affinity for paper and good durability led to these being the most popular dye class for ink jet applications. These dyes have been further modified to provide improved water fastness (replacement of sulphonic with carboxylic acid groups which can be protonated on the substrate).[5]



Direct Yellow 86

Typical dyes used in ink jet include Direct Yellow 86, Direct Yellow 132 and Direct Blue 199. These are generally more stable than acid dyes, in oxidative environments, and tend to be very substantive for hydroxylated substrates and cationic coatings.

Further modifications to these structures have included adding fixing groups such as piperazine which greatly enhances the interaction with the glucose groups within cellulose.[7] Modification to the direct dyes has led to improvements in light fastness, ozone fastness and humidity fastness. The direct dyes are more universally applicable in comparison with the acid dyes and can be effectively applied to many different coatings. They are very compatible to both the swellable polymer and microporous media. Direct dyes interact very effectively with polyhydroxylated materials such as PVOH, $Al(OH)_3$ However they also bind to PVP and gelatine where the H-bonding interactions provide a good surface for dye interaction.

Reactive Dyes

Further developments of ink jet dyes have involved the use of fibre reactive dyes which are capable of covalently bonding to textiles such as cellulose and wool.[2] The covalent bond provides the most stable interaction with a substrate and generally provides the most durable bonding interaction. To form such a dye..fibre bond in cotton the dye is applied at 80°C at pH >11. Until now it has not been possible to form a covalent bond in a commercial desk top ink jet system. For ink jet applications the reactive group is usually hydrolysed or capped with a nucleophilic group to give better ink stability.

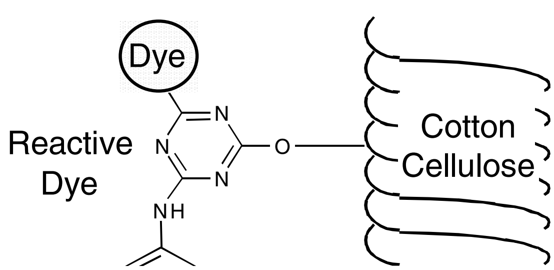


Figure 2. Covalently Bound Dye Molecule

The hydroxytriazine group provides very good affinity for H-bonding environments such as proteins, PVOH, alumina etc. In addition this group is effective in promoting dye…dye interactions leading to dye aggregation/crystallisation.

Photographic Dyes

Most of these dyes were water insoluble and were formed within a gelatine photographic emulsion.

The magenta dyes, based on gamma acid, were developed for their high light fastness and these contained sulphonic acid groups. These interact effectively with gelatine and provide very durable images.[6,7,10] On an alumina coating however, the gamma acid dyes can be susceptible to destruction by ozone.

Pigments

These are insoluble in water and have very little interaction with any of the different coatings. They tend to work better on microporous coating systems where the small pigment particles are partly absorbed into the pores in the surface of the coating however the absorption is limited due to the small pore size and the relatively large size of the pigments. Modified pigments have been developed where a charged group has been chemically attached to the surface of the pigment particle.[11]

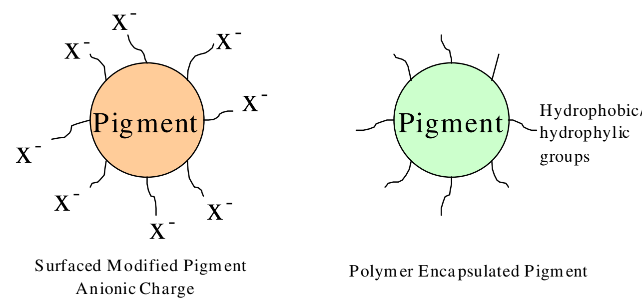


Figure 3. Surface Modified Pigments for Ink Jet

This provides an instant dispersion in water and leads to the possibility of some interaction with the media. Further modifications to the external surface of the pigments have involved including polymers with hydrophobic/hydrophylic groups which encapsulate the pigment.[12] This provides better durability and better compatability with the media. For the surface modified pigments then there are bonding interactions with the coating

PhotoPaper Design for Digital Imaging

Photographic image quality on desktop (SOHO) printers has improved very rapidly and most of the OEMs have now developed matched ink and media sets for photoprinting.

Photopapers

The most common type of ink jet photopaper is based on a resin coated support (Fig. 4). The two side PE coated paper is also the substrate used for silver halide photography.[5] This provides a very smooth durable substrate which has the look and feel of a traditional AgX photo.

The formulation of the receiver layers, applied to this surface, helps to determine the image properties.

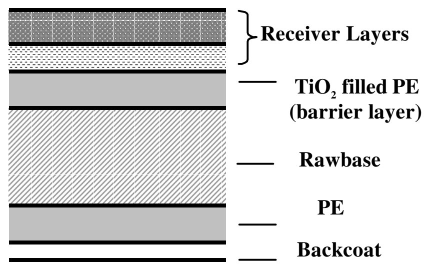


Figure 4. Resin Coated Photopaper for Ink Jet

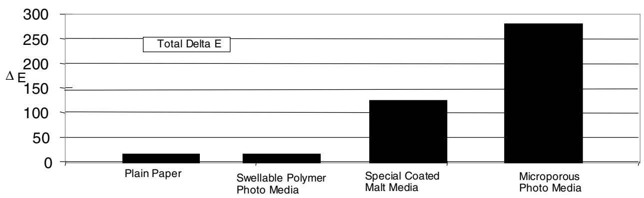


Figure 5. Ozone Fastness of Dyes on Different Media

The coating formulations need to be matched to the ink systems. The ozone fastness of dyes on different media is contrasted in *Fig.5.*The cellulose of the paper appears to provide good stability to ozone similar to a swellable polymer photomedia. The more porous silica environment of the matt coated paper reduces the ozone stability of the image and the microporous photopaper clearly demonstrates the worst ozone stability for the dyes due to the relatively open structure and the surface activation of the dyes to oxidation.

Coatings for Ink Jet

Swellable Polymer Type (Fig 6)

The water swellable polymers or binders typically gelatin, PVOH, polyacrylates etc absorb the inks by diffusion and interact with the dyes by electrostatic and H bonding in addition to Van der Waals forces dipole-dipole and other interactions. The dye molecules diffuse and spread through the coating layer(s) giving a good image quality, although the dry time may be slow. For pigmentary inks the pigment particles tend to remain largely on the surface with limited spreading of the ink.

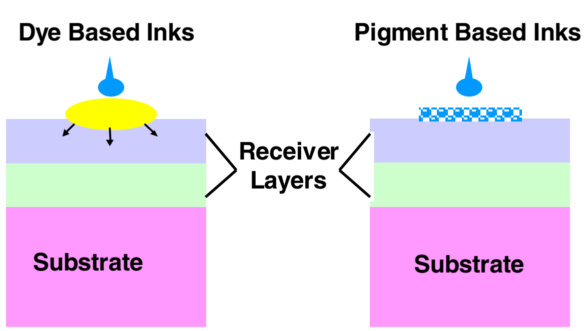


Figure 6 Interaction of Inks with Polymer Coatings

The image can readily be smudged by rubbing the surface of the print. The polymer coatings provide a high gloss surface similar to AgX and also very bright photo quality prints. As the speed of printers increases the rate of ink laydown is faster requiring a quicker uptake of ink by the coating. For faster printers and inks containing a high cosolvent loading or pigments, then the microporous pigment based media have been developed. The high gloss of the binder rich systems is a distinct advantage in comparison to the pigmentary microporous receiver layers. The swellable polymer coatings generally provide a more stable environment for yes and this is particularly true for ozone stability where the polymer effectively provides a physical barrier to ozone penetration (*Fig. 7).*

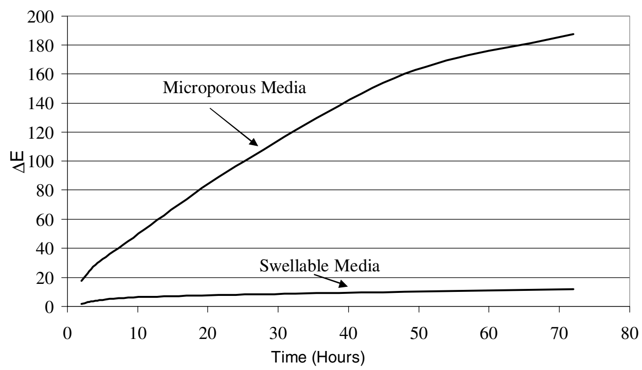


Figure 7. Ozone Fastness on Different Photomedia

Microporous Type (Fig. 8)

These have been developed for rapid ink uptake. They contain submicron alumina(cationic surface at pH<9) and silica(normally cationically surface modified)[4] based oxides to form a porous coating capable of instantly absorbing the ink by a capillary absorption process. The dyes are fixed to the cationic surface of these oxides. Pigment inks are more compatible with this type of media however the drytime is generally not as fast as that for dye based inks and there can still be problems associated with the physical interaction between pigment and media which leaves most of the pigment at the surface of the photopaper. Some typical problems which result from this surface interaction are differential gloss, bronzing and smearing.

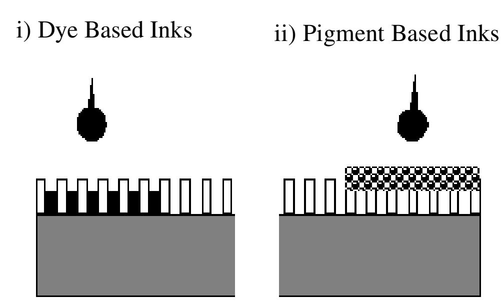


Figure 8. Interaction of Inks with Microporous Layers

The solution for these can come from further development of the inks and in addition the modification of the media coating to provide better compatability to the pigment inks. Comparison of the ozone stability of dyes and pigments on a microporous media indicates that the pigments demonstrate very good durability over prolonged exposure to ozone (*Fig 9).*

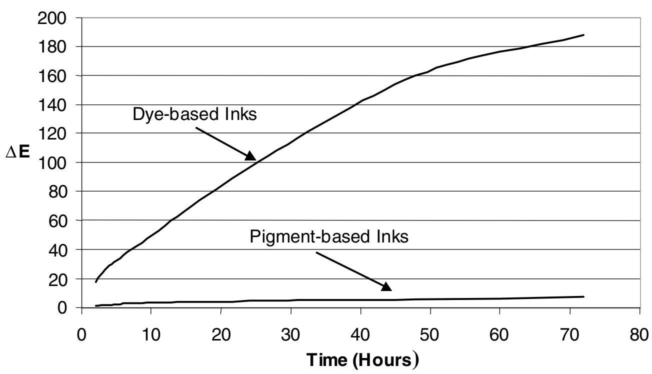


Figure 9. Ozone Fastness of Dyes and Pigments

Experimental

Optical density and L*a*b* of the colour blocks were recorded using an X-Rite Color Digital Swatchbook, model DTP22, X-Rite Inc, Grandville, USA.

Papers were printed in an environment of 23°C, 50% RH and allowed to dry for 8h under these conditions prior to any L*a*b* or OD measurements. ΔE was determined from the difference in L*a*b* before and after fading, and is determined by the following equation:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

Ozone Test:

Samples were exposed in an enclosed ozone chamber (Textile Innovators Corporation) at an ozone level of 3.5ppm over a specified time(e.g.24 hrs). Temperature was 23 °C and 50% relative humidity.

In addition further ozone testing was carried out using a 1ppm M287 Ozone Test Chamber (SDL International Textile Testing Solutions) same conditions as above.

Conclusions

By selecting a coating which can recognise the different ink systems, used in ink jet printing, a more stable environment can then be provided for the different colourants. The gelatine coatings, used in many of the swellable polymer photopapers, can already provide a very stable substrate for many of the current inks.

The development of new dye systems for ink jet has improved the interaction with the substrate and enhanced the durability properties. Thus by including groups, within the dye structures, which increase the interaction with the substrate/coating the durability properties can be improved.

Pigment inks have been developed to overcome many of the durability issues however these can only interact with the coating by a physical interaction. The surface modification of the pigments has increased the ability of the pigment inks to bond to the coating and the inclusion of charged groups or hydrophylic/hydrophobic groups provides a better interaction with the media. There are however some limitations for the pigment inks(particularly the image properties at the surface) and the dye based systems still offer the best match to AgX.

Ink jet ink systems have progressed considerably since the early introduction of the first colour dyes which gave bright colours on plain papers. The latest systems have been much more effectively matched and these devlopments will most likely continue until AgX quality levels are more closely matched by the digital imaging systems.

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Biography

Aidan Lavery received his BSc & PhD in chemistry from Queen's University Belfast(1980&'84). He carried out postdoctoral studies on transition metal chemistry at Edinburgh University before becoming a lecturer in Chemistry at Huddersfield University. In 1988 he joined ICI/Zeneca, where he spent 11 years. He became Group Leader for the Physical Science team developing ink jet systems. In 1999 he took up his current position with Felix Schoeller Imaging as Head of R&D for media development. Interests include ink/media interactions.