Issues in Ink Jet Image Stability

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Abstract

The Breadth of Uses in Ink Jet Leads to a Variety of Different Image Stability Issues

In this paper we discuss what some of the current major issues are in ink jet imaging. Because ink jet is used in a huge variety of applications, the articles produced are exposed to a large diversity of conditions. Different consumers, often using the same basic technology, require different properties.

Images produced by ink jet technology can be effected by light, water, humidity and many other factors, some previously unconsidered. How much progress is possible in addressing these issues? What strategies should be employed to solve them?

We describe approaches to solving some of the well-known issues such as light and water fastness, as well as some of the newer ones, such as humidity and ozone fastness.

Introduction

Ink jet is the only known primary printing technology. Images are described and constructed digitally, without any secondary processes not related to image production such as development, fusion, fixing, or impact. This simplicity gives ink jet huge advantages in digital printing, such as cost, speed, and quality.

Companies such as HP, Canon, and Epson have rapidly developed and improved this technology over the past 20 years, and an army of other companies, large and small, have also seen the potential of ink jet and made their own innovations, modest and ambitious. The inherent simplicity of ink jet, together with the application of all the innovators' ideas, has meant articles produced by ink jet finding their way into a large diversity of situations, from home office printing to textiles, from digital press to photographic printing - ink jet has been hugely successful.

The combined simplicity and diversity of ink jet usage do not come without their potential problems however. Inherent in the simplicity of the process is that the image is left to dry exposed on the surface of the substrate, open to water, light and other elements. Inherent in the diversity of applications is that the image is expected to fulfil a wide range of expectations. For example, for the home consumer, on one day their printer might be expected to produce text and vivid colors on plain paper, with little need or expectation of permanence to light but the need for smudge, rub and water fastness (examples of an immediate and catastrophic change in the image). On the same day, a photographic image might be printed with an expectation of glossy subtle tones with permanence to light, humidity and the air (examples of slow degradation of the image).

Ink jet articles produced for textiles, wide format, CAD, graphic arts *etc.* all have different issues in image stability requirements. How can some of these issues be addressed? And what set of properties in ink jet applications do users *really* value? Dry time? Image quality? Is lightfastness more important than say smudge fastness of text - and for which sectors and which consumers? For how many home consumers (or perhaps more importantly, for how many images) is cost more important that permanence? The debate over some of these questions will be a major factor in what drives the next round of innovations in ink jet.

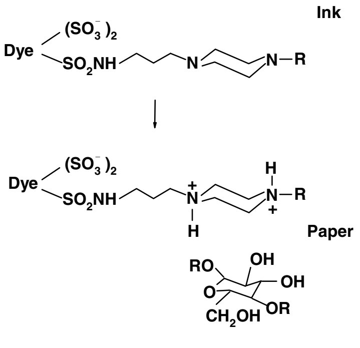
Some Obvious Aspects of Image Stability: (1) Waterfastness

For water-based inks, waterfastness can be a major issue. Because of the ubiquitous nature of water in everyday life, prints can come into contact with water from many sources, from sweaty hands to spots of rain to condensation on a cold drink. For plain paper, most users might not expect paper to retain its presentational excellence after such exposures, however it is an absolute necessity in home and office use that images retain a high degree of readability and integrity.

There are numerous methods of measuring fastness to exposure to water designed to mimic different conditions. The challenge for the chemist has been to design systems that have good operability and solubility/dispersability in the ink, but once on the paper do not re-dissolve or disperse on contact with water.

Avecia has used two successful approaches. The first was the pH switching dye mechanism. In this, dyes are substituted with carboxy groups, that solubilise the dye in slightly alkaline ink. Once printed on paper with a slightly lower pH, the carboxy groups on the dyes protonate to the insoluble form, and the dyes become very resistant to water. Dyes using this novel approach are very suited to printing in general use and especially on plain papers.

The waterfastness of such dyes can take some time to fully develop however, and there is a small amount of residual image instability on contact with water. We therefore sought a much faster mechanism that would give complete insolubility. This has been realised in what we term the CPI dyes, as depicted below. These probably operate by a zwitterionic type mechanism - protonation of the basic piperazine group leads to a zwitterion with virtually no water solubility, and the effect is instant.



Some Obvious Aspects of Image Stability: (2) Lightfastness

Lightfastness has been one of the most intensively studied properties of ink jet prints, especially over the last 2-3 years. The drivers for this has been the incredible gains in print quality made in inexpensive printer technology, as well as new specialised glossy media, and the contemporary development of the internet, digital cameras, home computer ownership & processing power, software sophistication *etc.* Taken together these recent advances have allowed for the possibility of digital printing of astounding quality photographic images.

Whilst offering numerous advantages over traditional silver halide processes, the images have, up to now, not been as fast to light as a silver halide produced image. There are several reason for this. Much recent research has focused on the interaction of the media with the dye, which can alter the lightfastness of an ink jet print by up to 100 fold. However before we consider this, we need to note that there are underlying reasons for lower lightfastness, which are to do with the ink jet process itself.

Photographic dyes are held in a protective gelatin layer, well below the surface, away from air and oxidants, whilst ink jet images are usually printed on less friendly surfaces. Even if printed on gelatin, dyes in ink jet images are more available to oxygen. Recent advances in media, with the use of microporous quick drying glossy papers being more common, have only made the demands on the dye greater - most dyes fade faster on these than on the less porous, more reductive environment of say, gelatin.

The generally lower lightfastness of ink jet prints when compared to photographic prints then, has not been due to inherently lower lightfastness chromophores being used. In fact the reverse is the case. If an ordinary photographic chromophore is used in ink jet the light fastness is much worse than when it is used in a silver halide process, and is generally much lower than the dyes used in ink jet now. Can dye and media systems which are much more robust to light be constructed? We believe yes; and have been investigating some approaches to this goal and demonstrated their success.

Before describing this some mention has to be made of the difficulties of measuring and even talking about lightfastness. Whilst other areas of colourant technological development such as textile dyes, photography, or say, pigments in plastics have long had established methods of testing products for lightfastness, in ink jet no such agreed standards yet exist.

Methods used in other areas can be a useful starting point, but are rarely going to be directly transferable. This is because the factors important to the fading process are often inherently different. For example in some colourant applications, depth of shade, humidity or secondary shades may be more or less important to the fading process than they are in ink jet, and so have been better or worse specified as part of the methodology.

Before being able to specify and control a methodology for measuring lightfastness then, all the important factors that have a bearing on the fading process have to be known and understood, and only recently have some of these factors started to become apparent.

Improving Lightfastness: Explaining Why Prints Fade

We have found that by far the most effective way of improving the lightfastness of a system is to understand the mechanism by which it fades, and to intervene in these. The impact the media has on lightfastness of the image is well documented. In terms of other factors such as the dye structure, these are known to have a dramatic effect, but the specific mechanisms are often patchily understood at best.

There are numerous reasons for this, which cannot be reasonably treated here, but an important point is that dyes rarely if ever have only one fade mechanism available to them. More often there is a whole group of mechanisms, and attempting to slow down one mechanism often accelerates another.

Some mechanisms have been investigated carefully in an ink jet context and this has proved useful in designing better dyes (see for example, Specialty Papers and Films 2000, DRC Conference, P Wight).

Probably the biggest factor in terms of dye design that impacts on the lightfastness is the chromophore chosen. The chromophoric type used (*e.g.* H-acid or gamma acid *etc.*) will have a dominant impact on the spectral characteristics and lightfastness achieved.

However the chromophore will not solely determine them. That this is so can be seen from the huge range of chroma and lightfastness achieved with the same dye, ink, and printer, when printing on different media. These often impose their effects by changing the physical form of the dye. In our hands, we have synthesised dyes from the H-acid class that span at least an order of magnitude in lightfastness and vary greatly in chroma. It is perhaps more accurate to say that the chromophore will impose certain boundaries on these key properties.

Understanding how the important chromophore classes fade, and having reliable methods for investigating the fading mechanisms of all chromophores on any given media is a key component in the research strategy for designing high lightfastness dyes.

Some Less Obvious Image Stability Issues

There are numerous image stability issues that are less obvious, some by virtue of them being specific to ink jet. Three examples of these with most relevance are catalytic fade, humidity fastness and ozone fastness.

Catalytic Fade

Catalytic fade happens when one dye has the property of catalytically degrading another one, which it is co-printed with. It is well described in colourant technology such as textiles. For example, when producing green textiles, it is common to use a mixture of a blue dye and a yellow dye. If the blue dye is an anthraquinone type, and the yellow is a pyrazalone type, the AQ fades the pyrazalone catalytically leaving only the AQ left - effectively the material changes from green to blue. This catalytic fade of the combined dye mixture happens faster than the inherent light fading of either component alone.

In ink jet it is possible to observe catalytic fade of magenta dyes by cyan dyes. The magenta dyes in question that seem most susceptible are the gamma acid types, and these can be faded if printed in a blue shade with phthalocyanines.

We believe that the phthalocyanines can produce small amounts of singlet oxygen by photo-sensitisation, which then goes on to oxidise the more vulnerable magenta dyes in an accelerated fashion. Having studied the exact mechanism of this oxidation, we have used two methods to solve the problem.

Table 1. DE of blue shades printed with an H acid dye and a gamma acid dye on a commercially available glossy film, using two different cyan dyes.

Sample/Dye type	H-acid Magenta	Gamma acid Magenta
Standard Cyan	14.8	23.53
Novel Cyan	9.03	6.71

One is to make more resistant gamma acid dyes, and the second is to make phthalocyanines that do not sensitise oxygen. The first approach has been partly successful, in that we have been able to make gamma acids that show reduced, but not absent catalytic fade with phthalocyanines. The second, in which we modify the structure of the phthalocyanine to prevent singlet oxygen sensitisation has been simpler and the table above shows that this problem can be effectively solved.

Humidity Fastness

Humidity fastness is the durability of an image under conditions of high humidity, perhaps also at a somewhat higher temperature than normal. It is usually specifically a problem for glossy films and papers, and happens as the dye diffuses through the media, rather like chromato-graphy. Compared to a say lightfastness, it is a relatively simple phenomenon, and is easily related to predictable properties of the dye in question. It is usually therefore a relatively easy phenomenon to deal with from the dye design aspect.

Ozone Fastness

Ozone fastness is (to date) only a potential issue; there is an hypothesis that prolonged exposure to ambient levels and occasional elevated levels of ozone can cause significant fade of ink jet prints that do not happen under other circumstances. The discussion has focused on peculiar fading of cyan dyes.

Our evaluations have shown that ink jet prints can be faded by increased levels of ozone, but this has stopped short of demonstrating (so far) that ozone is an unambiguous cause of fading in the “real world”. Further we find that two factors impact greatly on the level of fade observed when prints are exposed to increased levels of ozone. These are humidity and the media.

Increased levels of humidity cause generally much worse fading of cyan dyes for the same level of ozone. The media can also have a huge impact, some media inducing large fades, whilst others give a protective effect.

Sample	Substrate	% OD Loss	DE
Control CYAN	Company A	67.9	38.7
	Company B1	51.6	25.3
	Company B2	38.4	24.7
	Xerox Acid 4024	2.6	3.3
Dye1	Company A	23.3	9.4
	Company B1	34.3	16
	Company B2	20.8	17
	Xerox Acid 4024	4.3	1.3
Dye2	Company A	2.4	0.75
	Company B1	4	1
	Company B2	13.5	13
	Xerox Acid 4024	5.2	2.4
Dye3	Company A	2	1.4
	Company B1	3	1.5
	Company B2	7.2	12.5
	Xerox Acid 4024	3.9	1.7
Dye4	Company A	2.4	0.85
	Company B1	42	20
	Company B2	29.3	20
	Xerox Acid 4024	7.4	4.5

In terms of dye design, we have been able to apply the trends we have observed in these ozone experiments to develop radically more resistant dyes. The table above shows a series of our novel cyan dyes with very much better fastness to ozone, printed on commercially available media.

Conclusions

A range of image stability issues exists in ink jet as a direct result of the simplicity of the printing process. These create great demands on the development of new systems. A useful solution is very much more likely to be arrived at by a holistic approach of media, ink, head design, colourant *etc.* than by trying to consider each alone.

In addition, a scientific approach is vital in understanding the problem, and a entirely open minded creative approach to solving it - preferably unconstrained by existing ways of doing things, whether the problem is waterfastness, lightfastness or ozone fastness. Alternative approaches to developing innovative products are available, voodoo witchcraft and shamanism among them, but a scientific method is the only one with demonstrable success so far!

We also need to be constantly aware of the final customers real needs and how they are changing, and that in so far as any product is a collection of compromises, we need to focus on the customers' true priorities.

Using these strategies, much progress has been made in understanding and solving some image permanence issues, but much more progress is needed before ink jet's potential can be fully realised.

References

1. P Gordon and P Gregory, Organic Chemistry in Colour, Springer-Verlag.
2. P Gregory, High Tech Uses of Organic Colourants.
3. See, for example, H Wilhelm, WIR www.wilhelm-research.com

Biography

Paul Wight received his B.Sc. in Chemistry from Durham University (UK), in 1986, and a Ph.D. in Organic Chemistry from Nottingham University in 1989, where he studied synthetic organic chemistry, mechanisms of organo-cobalt radical reactions, and molecular modeling.

He joined ICI in 1989 and has stayed with the company throughout its various incarnations up to its present day Avecia form. He has worked on a wide variety of organic colourants, including disperse dyes and novel chromophores, and for the past six years has been working in various areas within ink jet.