

# Image Stability of Dye Diffusion Thermal Transfer Images

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## Abstract

As with the output from any reprographic technology it is the colour and general appearance of the printed image which is immediately most apparent to the end user and in this respect dye diffusion thermal transfer (D2T2) images are no exception. This may be an obvious statement but what people are really focusing their attention on is an aspect of the colourant, in this case dye, performance. First impressions are clearly important and can significantly influence the observers attitude to the technology. Assuming that an at least favourable initial reaction is achieved it isn't long before a more critical appraisal of the image starts to be made. Image (print) stability rapidly becomes an essential criterion and key determinant in the success of the technology. In the case of D2T2 images two important aspects of image stability are those related to mechanical handling and exposure of the print to light. This paper will consider both of these aspects but primarily the latter.

## Introduction

Although early predictions that D2T2 would eventually replace conventional silver halide photographic prints have proved to be erroneous the technology has continued to develop and establish itself as a means of producing photographic like images. It is highly likely that this lower than predicted impact is in no small part due to the time it has taken to develop digital cameras capable of capturing the very high quality images that we are accustomed to from conventional cameras. Though major improvements in digital cameras are fast becoming an almost daily occurrence they are somewhat late for D2T2 and the delay has allowed competing, low cost technology such as ink jet to develop and threaten the place of D2T2 in photo realistic imaging. None the less D2T2 continues to find application in niche areas and is likely to continue to do so. To simply maintain its current position it has been necessary to address several D2T2 image stability issues. Two of these, the resistance of the image to physical handling and to photochemical fading (light fastness), are considered in this paper.

## Dye Environment

The stability of D2T2 prints in terms of handling and light fastness are both strongly related to the location of the dye in the print media. The reasons for this become apparent on consideration of the environment in which a D2T2 dye is expected to exist. Despite the total thickness of the receiver sheet being several tens of microns the actual receiving layer is generally less than ten microns thick and the dye itself actually resides in the top few microns of this (Figure 1). This is a consequence of the dye transfer mechanism which has been described elsewhere<sup>1</sup>. The dye is therefore readily exposed to the effects of external agents.

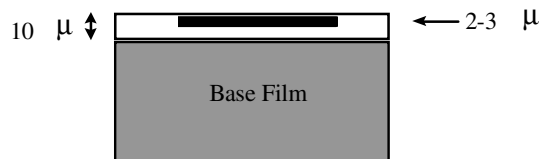
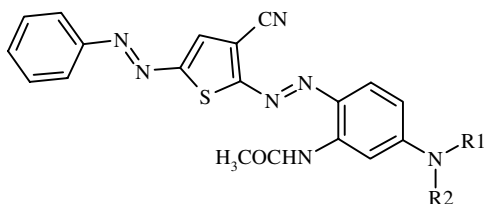


Figure 1. Dye Environment

## Physical Handling

Whenever the printed image is handled under normal circumstances there will inevitably be contact and subsequent contamination of the printed surface with finger grease. This grease can penetrate the receiver layer allowing dye molecules to migrate and may manifest itself as a deterioration in image quality. In some cases over a protracted period of time nucleation may be induced resulting in crystallisation of the dye within the receiver layer. This is observed initially as a loss in optical density and in more severe cases a clear finger print may be observed. In the important class of cyan dyes, the disazothiophenes,<sup>2</sup> this tendency was readily minimised, and as a consequence print stability enhanced, by making a relatively simple structural modification, the introduction of branched alkyl groups into the dye (Figure 2.). The performance of dyes in this respect is easily assessed by contacting the prints with finger grease, subjecting them to accelerated storage conditions and then determining the loss in optical density.



<u>R1</u>	<u>R2</u>	<u>% OD Loss</u>
C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	23.2
n-C <sub>4</sub> H <sub>9</sub>	n-C <sub>4</sub> H <sub>9</sub>	18.6
s-C <sub>4</sub> H <sub>9</sub>	n-C <sub>4</sub> H <sub>9</sub>	0.6

Figure 2. Effect Of Branching on Print Stability

### Light Fastness

As will be appreciated from the description of the D2T2 dye environment above the dye is clearly readily exposed to the effects of light and the atmosphere which in combination can lead to photo degradation of the dye. This may be contrasted to the situation in which the same dye exists in a textile application. In a polyester fibre the dye is present homogeneously throughout a fibre a hundred or more microns thick. Thus it can be appreciated that whereas fading of the top few microns of dye in a fibre would be barely discernible, the effect on a D2T2 print can be catastrophic. Hence many dyes which have acceptable light fastness when used to colour polyester textiles are unsuitable for use in the relatively harsh environment created in the polyester receiver layer of a D2T2 print. Additionally, since the majority of D2T2 images are printed onto a white substrate the light effectively has two opportunities to cause fading since any light not initially absorbed by the dye may be reflected back from the white underlying base film and may then have a second chance to initiate degradation.

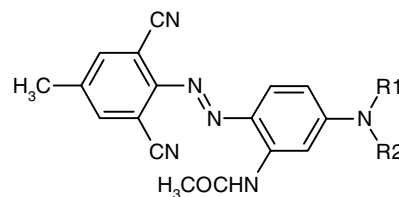
There has been an ongoing desire to enhance the light fastness of D2T2 prints and a number of approaches have been explored including passage of the printed image through a set of heated rollers in order to diffuse the dye further into the receiver layer. Incorporation of UV absorbers into the receiving layer of a D2T2 print has met with little success. An explanation for this lack of effect lies in the fact that in order for a UV absorber to be effective relatively high concentrations are usually required and needs to be located between the dye and the incident UV light. Clearly with the dye residing virtually at the surface of a D2T2 print the dye has at worst an equal opportunity to absorb the light and is therefore capable of competing very effectively with the UV absorber.

Greater success has been achieved by utilisation of a polymer layer which is applied as an overcoat onto the surface of the print following transfer of the dyes. This

clearly decreases the proximity of the dye to the print surface and enhances the light fastness. (An added benefit is that this would also obviate the physical handling problems referred to above). Inclusion of UV absorbers into this layer can be much more effective as they are now more advantageously located relative to the dye. It is possible to apply this layer by a transfer step within the thermal printer. However, there is a penalty to pay in terms of increased printing times and the need to manufacture more complex donor sheets. Hence commercially this is not a particularly attractive solution. For similar reasons post lamination of the print is also an unattractive proposition.

The inherent properties of the selected dye are therefore still a very important factor in determining the light fastness of a print and considerable effort has been expended in the search for improved dyes. When developing dyes for use in D2T2, as well as making a selection based on such important properties as shade, brightness and high tinctorial strength the light fastness properties are usually routinely evaluated using accelerated fading conditions. Whilst several chromogens may display the required shade attributes the inherent light fastness properties vary significantly.

It is known that incorporation of electron withdrawing groups into the N,N-dialkyl groups of the coupling components of azo dyes can significantly enhance the light fastness properties<sup>3</sup>. (Figure 3). This effect is believed to arise from the consequent reduction in electron density at the nitrogen atom due to the inductive effect of the electron withdrawing group.



<u>R1</u>	<u>R2</u>	<u>% LF*</u>
C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	44.4
C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	1.8

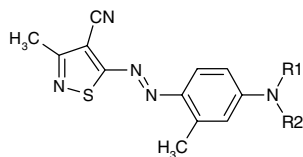
\* Refers to % loss in optical density

Figure 3. Influence Of Electron Withdrawing Groups On Light Fastness.

Unfortunately however, introduction of electron withdrawing groups in this way also leads to a marked hypsochromic shift in the absorption maximum of the dye and a dye of considerably different shade may result.

This shift in shade can mean the dye is no longer particularly suitable as, for example, a magenta and necessitates further dye design. During the course of our research into suitable dyes for D2T2 we considered that, if we were able to determine the nature of the photodegradation products, then we may be in a better position to design dyes of improved light fastness. The outcome of this work resulted in the identification of a simple structural modification, applicable to a wide variety of D2T2 dyes, which confers enhanced light fastness properties without detriment to shade.

Several samples of a commercially available receiver sheet were printed with the excellent isothiazole derived D2T2 dye, **1**. The prints were then subjected to accelerated fading in an Atlas Ci35 weatherometer (0.8Wm<sup>2</sup>, 45°C black panel temperature, 50% RH). After 100hrs the prints were removed and the residual dye together with the photo degradation products extracted into acetone. The mixture of products obtained was separated by preparative thin layer chromatography. Two main bands were obtained and following extraction from the silica gel these were analysed by mass spectrometry. The minor constituent was found to correspond to unchanged dye **1**, and the other, main, band to the dealkylated product **2**.



Dye	R1	R2	$\Delta E(24hrs)$	$\lambda_{max}$
1	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-	-
2	H	C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-	-
3	n-C <sub>4</sub> H <sub>9</sub>	n-C <sub>4</sub> H <sub>9</sub>	6	553nm
4	n-C <sub>4</sub> H <sub>9</sub>	s-C <sub>4</sub> H <sub>9</sub>	2	554nm

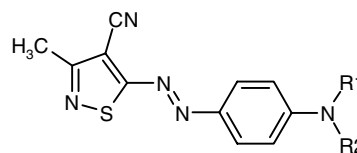
Figure 4. Light Fastness & Fading Products Of Isothiazole Dyes

The structure of the isolated photodegradation product is commensurate with the observation of a hypsochromic shift in shade on fading and also with the observation that the fading of azo dyes on polyester textiles involves a dealkylation step. Concurrently with this work we were continuing to routinely determine the light fastness properties of other D2T2 dyes synthesised as part of our ongoing research efforts. During this work we were surprised to notice a significant difference in the light fastness properties of the two isomeric dyes, **3** & **4**. It is interesting to note that the higher light fastness dye, **3**, containing the  $\alpha$ -branched alkyl group, experiences no reduction in electron density at the nitrogen atom compared to the di-n-alkyl isomer, **4**. If anything the electron density at the nitrogen atom would be expected to be slightly higher due to the inductive effect of the methyl group. Furthermore the two dyes exhibit virtually identical

absorption maxima. This result raised the question of whether this was simply an isolated example or part of a more general trend. Hence a series of isothiazolyazo dyes with and without  $\alpha$ -branching were synthesised and their light fastness properties studied. The results confirmed that when the isothiazolyazo dyes contain an  $\alpha$ -branched group the light fastness is always higher.

We were then encouraged to determine if the light fastness enhancement due to the presence of the  $\alpha$ -branched group was in addition to any improvement obtained by reducing the electron density at the nitrogen atom or would the electronic effects override the steric effects.

Using the dyes **5**, **6** & **7** confirmed the fact that the inductive effects due to the presence of the electron withdrawing acetoxy group enhance the light fastness but also show that steric factors arising from the  $\alpha$ -branching provide a further enhancement (Figure 5).



Dye	R1	R2	$\Delta E(48hrs)$
5	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	11
6	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	6
7	C <sub>2</sub> H <sub>5</sub>	CH(CH <sub>3</sub> )CH <sub>2</sub> OCOCH <sub>3</sub>	3

Figure 5. Combined Effect Of Branching & Electron Withdrawing Groups On Light Fastness.

Further studies were carried out using dyes derived from diazo components other than 5-amino-4-cyano-3-methyl-isothiazole. Again we found that the presence of an  $\alpha$ -branched substituent on the N,N-dialkylamino donor group of the coupling component resulted in significantly enhanced light fastness. Having demonstrated that this structural modification appeared to be applicable to azo dyes derived from para coupling N,N-dialkylarylamines in general, our next step was then to determine if the effect was observed with other chromogens which are useful as D2T2 dyes. Amongst those to which we suspected the  $\alpha$ -branching modification might be applicable were magenta dyes of the tricyanovinylarylamine type, methine yellows, methine cyans and indoaniline cyans. The results obtained demonstrated the wide applicability of  $\alpha$ -branching as a means of improving light fastness in non azo dyes. As was the case with the isothiazolyazo dyes described earlier the improvement is achieved without substantially affecting the absorption maxima of the dyes relative to the non branched isomers and homologues.

Having established the fact that the presence of  $\alpha$ -branching leads to advantageous light fastness properties we extended the photofading studies carried out at the beginning of this work in order to determine the nature of the degradation products. In all the examples studied we found that dealkylation occurred and that in each case the  $\alpha$ -branched group was retained.

Despite the difficulties encountered in determining the photofading products of azo dyes in a textile application a mechanism for the fading process has been proposed<sup>4</sup>. The photo degradation products isolated in our studies support this mechanism and provide the additional evidence that when an  $\alpha$ -branched group is present and dealkylation occurs, it is the  $\alpha$ -branched group which is preferentially retained.

### Conclusions

The presence of  $\alpha$ -branched groups in the N,N-dialkylamino substituents of a range chromophores improves the light fastness properties of such dyes when used in the D2T2 application. This simple structural modification has little or no effect on the absorption maximum of the dye and therefore negligible effect on the shade of the dye. The photofading products are in agreement with D2T2 dyes fading via an oxidative

dealkylation process and, when one of the N,N-dialkyl groups is  $\alpha$ -branched this group is preferentially retained. The probable reason for this effect is that the branched group sterically hinders attack of singlet oxygen on the nitrogen atom and/or hinders abstraction of a proton from the  $\alpha$ -carbon atom.

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