Lightfastness Performance In Digital Imaging: The Role Of Dye-Dye And Dye-Polymer Interactions

A. A. Clifton, N. Nugent
(ICI Imagedata, Brantham Manningtree, Essex, CO11 1NL)

Abstract

Digital imaging technologies have progressed significantly over recent years to the point where modern hard copy output from dye diffusion and more recently ink-jet printers can be compared, in terms of image quality at least, with silver halide. Despite these advances in the print quality, image preservation remains a key technical challenge. In particular the preservation of images during exposure to light continues to attract much interest.

The light stability performance of a series of hydroxyl functional azo dyes, in which the functional groups were electronically isolated from the chromophore, has been studied in a range of polymeric hosts. In these systems three distinct interactive dye species have been identified by infra-red spectroscopy; dye-dye, dye-polymer and intra-molecularly bonded dye molecules. The relative proportion of each has been shown to be dependent on the concentration of dye, the number of functional groups on the dye molecule and the ability of the host polymer to take part in hydrogen bonding with the hydroxyl groups. The amount of fading exhibited by these systems has been correlated with the concentration of dye, the dye-polymer interaction strength and the number of functional groups present on the dye. Thus, it has been shown that the amount of fading is strongly dependent on the proportion of dye-dye to dye-polymer species with higher levels of dye-dye interaction promoting fading.

Introduction

Most high quality, 'Photo realistic', digital output systems are currently based on solvated dyes, molecularly dispersed in the imaging media. Optimising the light stability of such dye in polymer images is a non-trivial issue and requires a detailed understanding of a number of material and environmental factors as outlined in figure 1.

Previous workers have reported that dye-dye interactions or aggregation in imaged systems leads to an increase in the light stability.[1-3] Indeed, it is well known in ink-jet printing that pigmented inks give rise to longer print lifetimes when exposed to light. Conversely, it has been reported in dye diffusion printing that high levels of dye present at the surface of a printed image results in poor image stability and in particular, light stability.[4]

The current paper looks at the light stability of a number of solvated dye in polymer systems where the chromagen has been electronically isolated from hydrogen bonding hydroxyl functional groups. The proportion of dye-dye to dye-polymer interacting species has been measured by infrared spectroscopy as reported previously.[5]
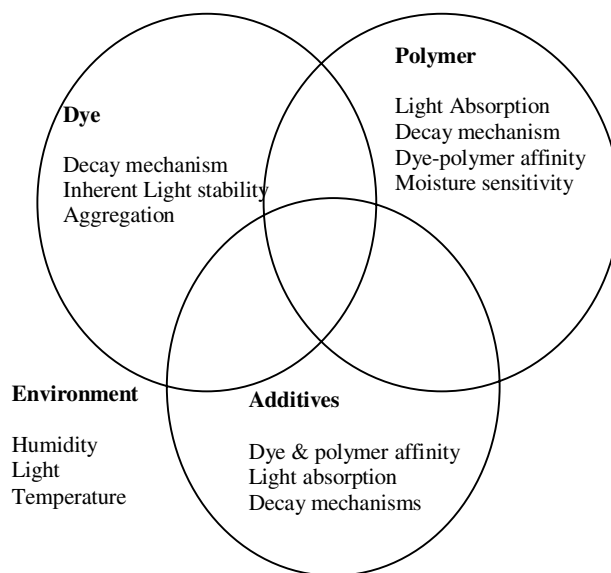

Figure 1 Factors influencing light stability of dye in polymer systems

Experimental

The dyes used in the current study were all based on the simple diazo chromagen shown below. The number of functional groups present on the molecule was varied from 0 to 3 as described in table 1.
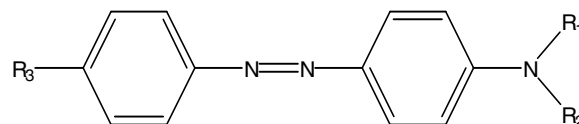

Figure 2. Basic cromagen structure

Table 1: Dye Structures

	R1	R2	R3
Y0	C_3H_7	C_3H_7	C_2H_5
Y1	C_3H_7	C_3H_7	C_2H_4OH
Y2	C_2H_5	C_3H_6OH	C_2H_4OH
Y3	C_3H_6OH	C_3H_6OH	C_2H_4OH
Y2A	C_2H_5	C_3H_6COOH	CH_2COOH

Table 2. Polymers used in the current study

Polymer	Type	Abbreviation
Vylon 103	Polyester	Vy103
Poly(vinyl pyridine)	Amine	2PVPy
Poly(vinyl acetate)	Ester	PVAc
Poly(vinyl chloride)	Non-functional	PVC
Polystyrene	Non-functional	PS

Dye-Dye vs Dye-Polymer Ratio

Pre-determined quantities of dye and polymer were weighed out and dissolved in spectroscopic grade tetrahydrofuran to give an 8% by weight solids solution. Pure, polymer only solutions were made up in the same way. Drops of each solution were placed on separate NaCl plates and dried under an IR lamp at 70 degrees for 5 minutes. Infra-red spectra were recorded on a Perkin-Elmer 1720x FTIR spectrometer. The resolution was set to 2cm^{-1} and the spectra were signal averaged over 10 scans. The relevant pure polymer spectrum was subtracted from each of the dye-polymer spectra to give spectra of the dyes in the host polymeric environment. The dye-dye and dye-polymer peaks were identified and proportion of d-d/d-p was calculated from the ratio of the hydroxyl band intensities for each species present.

Lightfastness Measurements

Samples were prepared as for IR measurement except the dye in polymer solutions were used to wire bar coat films onto Melinex 990. In all cases the percentage solids in solution and the wire bar were varied in an attempt to achieve a constant optical density value of one for the coated film.

Accelerated light fading was carried out using an Atlas C35i fadeometer operating with a xenon arc lamp. Conditions were set to an irradiance of 1.5 Wm^{-2}, total exposure of 388.8 W, at a relative humidity of 50% and a temperature of 60°C. The amount of fading was measured after, 12hrs and 24hrs. In each case, the optical density values were recorded using a Gretag SP5 spectropho-tometer operating with a D65 illuminant. From this data percentage optical density loss (%OD) were calculated.

Results and Discussion

Slark and Hadgett sudied the behaviour of simple hydroxyl functional dye solutes in an amorphous polyester matrix.[5]

They showed that the frequency and intensity of the dye hydroxyl stretching band was dependent on the nature and type of the interaction between the dye and polymer. Indeed, three different interacting species were identified, dye-dye, dye-polymer and dye intramolecular interactions. This technique has been used in the current work to assess the relative proportion of each of these species over a wide range of dye concentrations in a number of polymers. The results of this investigation are presented in table 3 and the data for Y2 dye in three different polymers is shown in figure 3.

Table 3

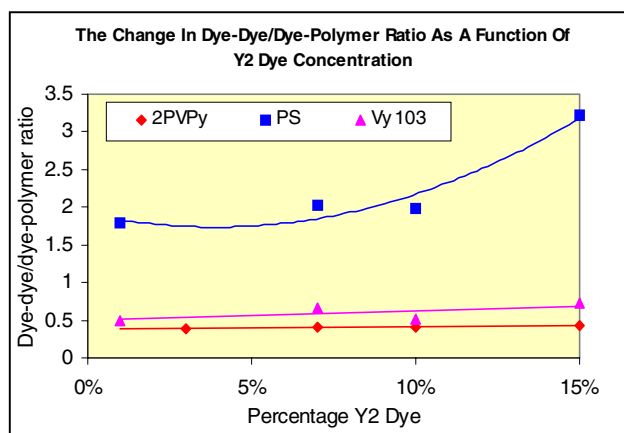| Dye	Polymer	[Dye]	d-d/d-p
Y1	2PVPy	10%	-
Y3	2PVPy	10%	0.49
Y2	2PVPy	1%	-
Y2	2PVPy	3%	0.38
Y2	2PVPy	7%	0.41
Y2	2PVPy	10%	0.40
Y2	2PVPy	15%	0.42
Y1	Vy 103	10%	0.55
Y3	Vy 103	10%	1.08
Y2	Vy 103	1%	0.50
Y2	Vy 103	3%	-
Y2	Vy 103	7%	0.51
Y2	Vy 103	10%	0.67
Y2	Vy 103	15%	0.72
Y1	PS	10%	1.79
Y3	PS	10%	4.44
Y2	PS	1%	1.8
Y2	PS	3%	-
Y2	PS	7%	1.98
Y2	PS	10%	2.03
Y2	PS	15%	3.23
Y2	PVC	10%	3.45
Y2	PVAc	10%	0.37

Figure 3 Proportion of dye-dye vs dye-polymer species for Y2 dye at various concentrations in three polymers.

The data in table 3 and figure 3 clearly show a much greater proportion of dye-polymer species as the hydrogen bonding capability of the host polymer is increased according to the order PVPy>Vy 103>>PS. It is also evident that the relative proportion of hydroxyl groups involved in dye-polymer type interactions decreases as the concentration of Y2 increases for both polyester and polystyrene hosts. With poly(2-vinyl pyridine) there appears to be no change in the relative proportion of dye-dye to dye-polymer species as the dye concentration increases upto 15% by weight dye. This is thought to arise from the increased hydrogen bonding capability of this host polymer. Only a very limited amount of intra-molecular H-bonding was observed with the Y2 dye.

d-d/d-p Ratio vs Number Of Functional Groups
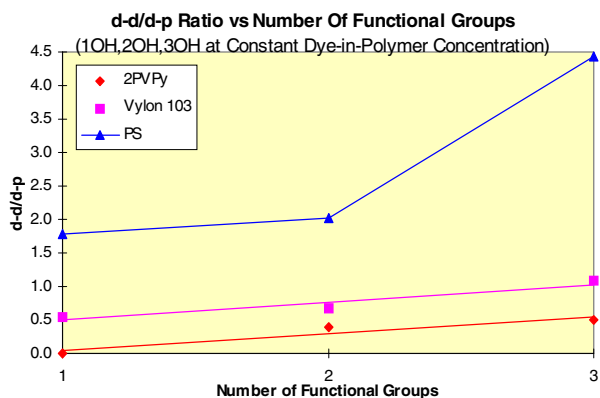(1OH,2OH,3OH at Constant Dye-in-Polymer Concentration)

Figure 4. The change in dye-dye to dye-polymer ratio as a function of the number of hydroxyl groups present on the dye. All data were obtained at 10% dye concentration.
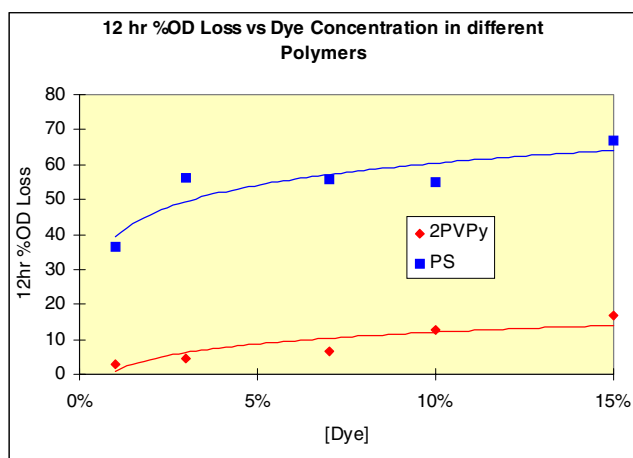

12 hr %OD Loss vs Dye Concentration in different Polymers

Figure 5 The percentage Y2 dye loss after 12 hours accelerated ageing in PVPy and PS hosts

From figure 4 it can be seen that as the number of hydroxyl groups on the dye is increased from 1 to 3 the proportion of dye-dye to dye-polymer species also increases in all polymer hosts. Once again the proportion of dye-

polymer to dye-dye species follows the order PVPy>Vy 103>>PS.

The 12 hour accelerated fading characteristics of the Y2 dye in polystyrene and poly(vinyl pyridine) are shown in figure 5. Clearly, Y2 dye fades much more readily in PS showing around 50% density loss at 10% initial dye concentration compared with only about 10% density loss in PVPy. In both host polymers there is a gradual increase the amount of dye lost as the concentration increases. For PS the dye loss ranges from 37 to 67% and for PVPy from 3 to 17%.

It is interesting to note that despite both polymers having a carbon backbone with pendant aromatic rings, PS gives rise to a 5 to 10 fold increase in the amount of dye lost. This is a particularly striking result as neither polymer exhibits significant absorption above 300 nm, the region corresponding to the output from the fadeometer. This trend is also maintained after 24 hours accelerated fading, as shown in figure 6.
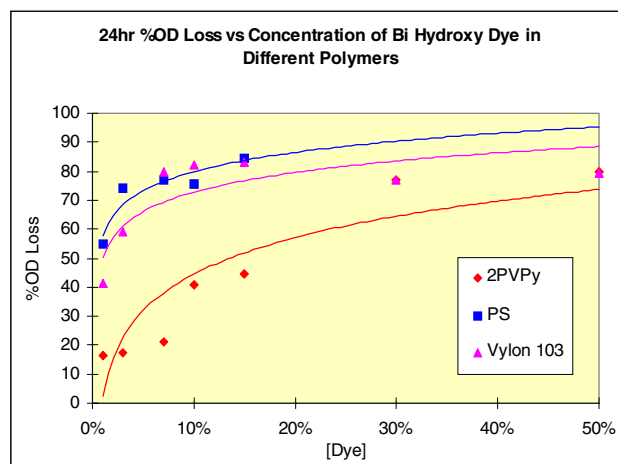

24hr %OD Loss vs Concentration of Bi Hydroxy Dye in Different Polymers

Figure 6. The percentage Y2 dye loss after 24 hours accelerated ageing in PVPy, PS and Vy 103 hosts

The difference in fading performance between PS and PVPy is less marked after 24 hours as nearly all the dye has faded in the PS host and so the data is asymptotically approaching 100% dye loss. Also shown in figure 6 is the fading performance data for Y2 in Vy 103 after 24 hours. It should be noted that despite having a lower proportion of dye-dye interactive species compared with PS, Vy 103 exhibits very similar levels of fading. This feature is more pronounced in figure 7 where the fading data has been correlated with the ratio of dye-dye to dye-polymer species present in each host polymer. The data for both PS and PVPy have been grouped together and after both 12 and 24 hours accelerated fading gives a good correlation between D-D/D-P ratio and the amount of dye lost. Vy 103, however, shows significantly more fading than would be expected if the level of dye-dye interaction was solely responsible for fading. This is most probably attributable to

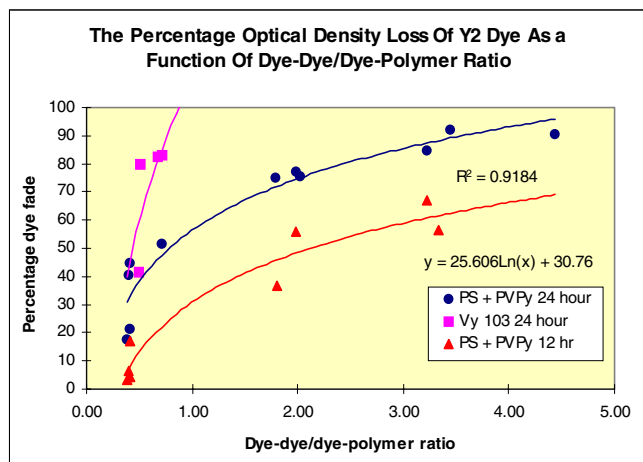light absorption by the aromatic backbone and ester carbonyl groups present in this polymer.

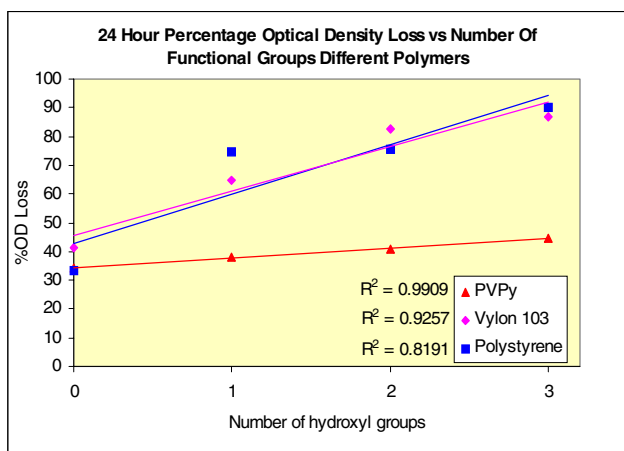*Figure 7. Percentage Y2 dye loss as a function of dye-dye to dye-polymer ratio.*

Figure 8. The percentage dye loss versus the number of hydroxyl functional groups.

The correlation shown in figure 7 strongly suggests a link between the light stability performance of a simple azo chromagen and the environment in which it is situated. Namely, the more the dye interacts with the polymer the less it fades. This result would seem to contradict the increasing body of data suggesting that dye-dye aggregation leads to increases in light stability. It should, however, be remembered that the hydroxyl functional groups are electronically isolated from the chromagen and therefore do not participate in the colour of the dye molecules. Neither are they likely therefore to contribute directly to any energy decay mechanism. Conversely, it can be argued that the hydroxyl functionality serves to promote 'head' to 'tail' type stacking of the dye molecules. This in turn would suggest that this arrangement is much less stable than free dye, possibly because energy transfer can occur from one dye to the next in the stack.

Further evidence for aggregation promoting fading with the current dyes can be seen in figure 8 which shows the 24 hour fading data for the series of hydroxyl functional azo dyes having from 0 through to 3 functional groups (Y0 to Y3). In all three polymers there is an increase in the percentage dye loss with increasing functional group density. Once again, PVPy gives rise to significantly less dye fade than Vy 103 or PS. It is interesting to note that when the dye has no hydroxyl group present (Y0) PS behaves very similarly to PVPy again suggesting that the inherent behaviour of these two polymers is similar.

Variation in Host Polymer

Since the amount of dye fading has been shown to depend on the proportion of dye-dye versus dye-polymer interacting species, the hydrogen bonding capability of the polymer should significantly influence the light stability. To verify this hypothesis the fading behaviour of Y2 dye in a series of polymers was investigated at 10% initial dye concentration. The results are shown in figure 9.
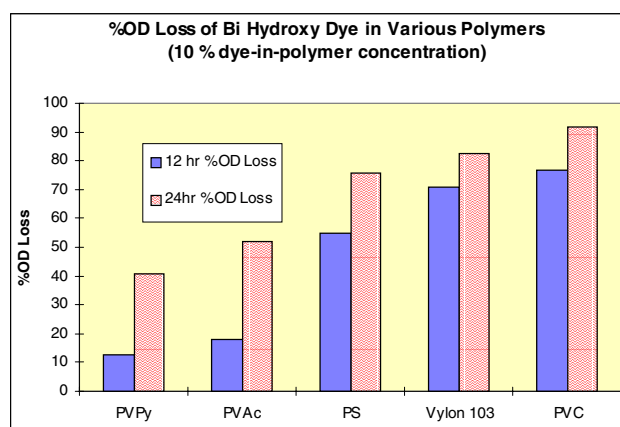

Figure 9. The percentage optical density loss of Y2 dye in a range of polymers after 12 and 24 hours accelerated fading .

The interaction of the dye hydroxyl group with a polymer gives rise to a frequency shift, which can be used as a measure of the interaction strength between the two. In this way it was found that the interaction strength for Y2 follows the order PVPy>PVAc>Vy 103>PS~PVC. From figure 9 it can be seen that the fading follows the order PVPy<PVAc<PS<Vy 103~PVC. Thus, although PVPy and PVAc follow this order and show the least dye loss, Vy 103 and PVC show more fading than expected. In the case of the polyester it expected that the ester carbonyl groups and aromatic backbone result in a greater amount of polymer assisted dye fading.

In order to extend this line of investigation further the fading performance of a bi-acid functional dye (Y2A) was studied in the same range of polymers. Although no equivalent infrared data is available for the acid dye, it is assumed that the hydrogen bonding capability should follow

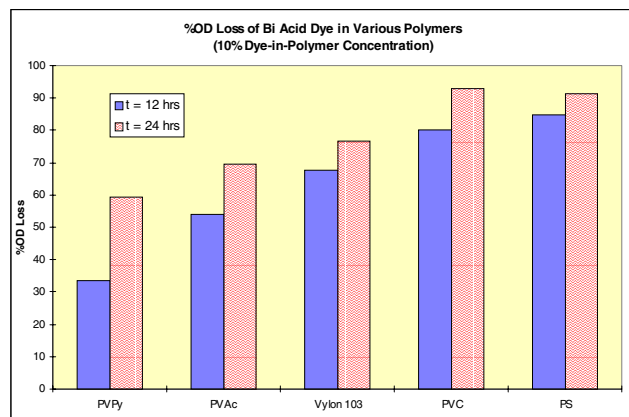the same order as the hydroxyl dyes. The fading results are shown in figure 10.

Figure 10. The percentage optical density loss of Y2A dye in a range of polymers after 12 and 24 hours accelerated fading.

Clearly, the amount of dye lost in each polymer follows the sequence of the expected interaction strength; PVPy<PVAc<Vy 103<PVC~PS. It is also worth noting that the percentage dye loss is greater in each polymer than observed with the hydroxyl functional dye. This would suggest that the acid functional dye has a greater tendency to self associate that the bi-hydroxyl dye in this range of polymers.

Conclusions

Increased dye-dye intermolecular association has been found to occur at higher dye concentration or as the number of functional groups increased. Dye-polymer species increase as the hydrogen bonding capability of the host polymer is increased.

The percentage dye lost during accelerated fading has been shown to correlate well with the ratio dye-dye/dye-polymer species present in polystyrene and poly(vinyl pyridine) hosts. Amorphous polyester (Vy 103) showed a

similar trend, but with much higher levels of fading for a give dye-dye/dye-polymer ratio.

Increasing the number and or strength of the interactive functional groups increases the amount of dye fading. Conversely, increasing the hydrogen bonding capability of the host polymer reduces the level of dye fade.

Although the light stability of a dye in polymer combination is complex and depends on both the dye and polymer properties, an equally significant contribution can arise from the arrangement of the dye in the overall structure.

Acknowledgements

References

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2.   P. Doll, F. Shi, S. Kelly and W. Wnek, IS&T NIP 14, 1998, pg. 118.
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Biography

Andrew graduated in 1990 with a BSc. degree in Pure Chemistry from the City University in London. From 1990 to 1993 he carried out research in the area of polymer surface modification for his PhD at the University of Bath. In 1994 Andrew was awarded a European community post-doctoral research fellowship and travelled to the Institute of Microtechnology (IMM) in Mainz Germany to study the role of polymers in deep lithography. Since 1995 Andrew has been working for ICI Imagedata, researching the fundamental applied property links in imaging media.