

New Colorants for Ink Jet Printing of Digital Images

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Abstract

The differing colour and fastness properties of dyes and pigments has predisposed the two classes of colorant towards different applications. This paper describes some work directed towards improving the fastness of azo dyes, whilst maintaining their superior colour properties in the yellow and magenta shade areas. The control of hydrogen-bonding offers a means for influencing fastness. Promotion of hydrogen-bonding interactions results in improved lightfastness, whereas the deliberate blocking of such bonding reduces fastness.

Introduction

With the continuing increase in printing of digital photographs, the need for print longevity has become greater than ever. This need for fastness to light and atmospheric oxidants is coupled with a requirement to retain acceptable shade and operability from ever smaller printheads. Aggregated dyes and pigments tend to exhibit enhanced lightfastness compared with disaggregated dyes¹ which usually give rise to brighter shades and offer greater flexibility in ink formulation. These differences in properties between colorants has resulted in them finding use in different applications. For use in printing digital photographs there is a desire to improve the fastness of dyes, whilst retaining their better colour properties. This paper describes some work directed towards improving the fastness of azo dyes.

A characteristic feature of pigments is the existence of non-covalent interactions including, for example, hydrogen-bonds and π -stacking, which produce particulate crystals with high lattice energies. In this paper we demonstrate that the disruption of hydrogen-bonding between hydrazone and triazinyl moieties increases the vulnerability of the dye towards destructive entities, i.e. disaggregation results in enhanced photofading on paper, whereas the promotion of hydrogen-bonding improves photostability.

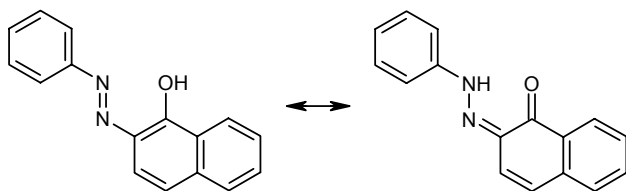


Figure 1. Tautomerism in 2-azo-1-naphthol dyes.

A Model System

The tautomerism of azo dyes derived from 1-naphthol, coupled in the *ortho* position, is well documented, especially by solution studies.^{1,4} Whilst such dyes adopt predominantly the hydrazone

tautomer, the position of the equilibrium is known to be influenced by pH, substituent effects, hydrogen bonding interactions and environment, e.g. solvent.

The importance of tautomerism on fastness is clearly illustrated with reference to the isomeric model dye Orange I, a commercially available dye which can adopt both azo and hydrazone tautomeric forms. The *O*-methylated derivative **1** and *N*-methylated derivative **2** were prepared, to serve as models of the azo and hydrazone tautomers respectively.

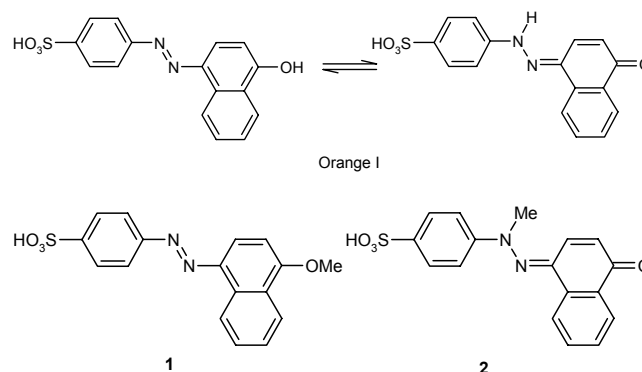


Table 1 shows the values of ΔE after 100 hours in an accelerated lightfastness test. It can be seen that the *O*-methyl derivative fades considerably less than Orange I, whereas *N*-methylation of the hydrazone tautomer has much less effect on lightfastness. It is known that the hydrazone tautomer is the most abundant, and the fastness of Orange I is closer to the hydrazone locked tautomer **2**.

Table 1: Lightfastness of Orange I Derivatives

Dye	ΔE (100 hours)	
	Xerox acid	Glossy Paper
Orange I	33	44
1 (O-Me)	16	21
2 (N-Me)	32	55

Towards Real Magenta Dyes

Acknowledging the significance of tautomeric form on the fastness of prints led to consideration as to whether tautomerism of groups removed from the colorant might offer a means to improved fastness. We wished to gain insights towards the enhanced lightfastness of dyes containing the hydroxytriazinyl motif, which features in several patents² describing magenta colorants from a number of organisations. This moiety can exhibit tautomerism (Figure 2) with extreme structures being a "heteroaromatic phenol"

and a cyclic urea (lactim). These tautomers have differing propensities to form hydrogen bonds. In the dyes studied, and in model compounds, the triazine group adopts a lactim structure as indicated by the characteristic carbonyl stretch (*ca.* 1713cm⁻¹) seen in the infra-red spectrum of solid samples.

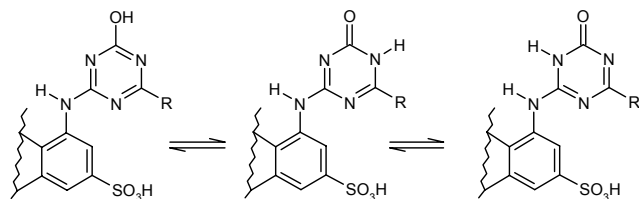
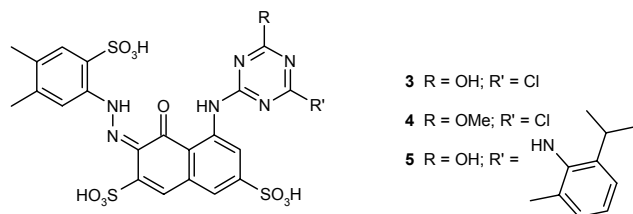


Figure 2. Tautomeric forms of the hydroxytriazinyl moiety.

It was reasoned that *intermolecular* hydrogen bonds formed in the solid state i.e. on the media would affect the fastness of prints, as they would influence the balance of which tautomer is formed. This could be the result of an effective local pH or by direct dye-dye or dye-media interaction. The monoazo magenta dyes **3-5** bearing triazinyl groups, typical of commercial ink jet magenta dyes, were synthesised using established procedures¹ to test whether a significant difference in fastness could be realised.



The dyes were printed from a simple ink jet ink formulation on paper and the samples faded in an accelerated test. The values of ΔE following 100 hours exposure are given in Table 2.

Table 2: The Lightfastness of Azo Dyes 3-5 Bearing Triazinyl Moieties

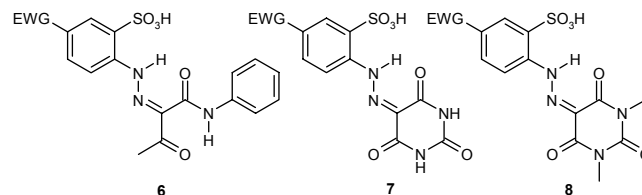
Dye	ΔE (100 hours)		
	Plain paper	Glossy Paper	Glossy Film
3	10	16	17
4	15	17	33
5	28	24	38

From the table it can be seen that the substituents on the triazinyl group have a marked effect on the lightfastness of the dye, despite being far removed from the chromogen. The implication is that modifications to the dye structure cause changes in the intermolecular interactions either with the paper or other dye molecules, which in turn affect reactivity i.e. photofading.

For full colour ink jet printing three subtractive primaries are required – yellow, magenta and cyan. The colorant of choice in the

cyan area is the phthalocyanine, where significant aggregation effects are noted together with good lightfastness, and these colorants are not discussed further here. For the yellow shade area, where azo dyes are most common, it was felt that increasing hydrogen-bonding may offer a means to improved fastness.

The Hansa yellow pigments display good fastness and so it was decided to explore solubilised examples, to ascertain whether the brightness advantage of dyes, could be achieved with improved fastness by an extended hydrogen bonding network. Three dyes **6-8** were prepared all containing a similar structure.



These dyes might be anticipated to have a differing ability to form intermolecular hydrogen bonds. Table 3 confirms that the lightfastness of these three dyes is consistent with this. The monoamide dye **6** has a lightfastness in between dye **7**, which possesses both hydrogen bond donors and acceptors, and dye **8**, where the only hydrogen available for hydrogen bonding is tied up in an intramolecular hydrogen bond.

Table 3: Variation in Lightfastness for Dyes with Differing Hydrogen Bonding Capability

Dye	ΔE (100 hours)
	Glossy Paper
6	15
7	4
8	31

Conclusion

The promotion of hydrogen bonding in different types of yellow and magenta azo dyes leads to enhanced fastness. Furthermore, the increased fastness of prints is attained without diminishing the bright shades, characteristic of these dye types.

Experimental

All compounds were characterised by ¹H NMR spectroscopy, electrospray mass spectrometry and combustion analysis. The data obtained were consistent with the proposed structures.

The dyes were printed from an ink containing by weight 3% dye, 2% surfactant, 10% non-volatile cosolvent and the balance water. Fading experiments were conducted in an Atlas Ci5000 Weatherometer for 100 hours. ΔE values are reported as the difference in CIELAB co-ordinates, measured with an X-Rite 938 spectrodensitometer, between a faded sample and an unexposed sample using the formula $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$. The error on such measurements is less than 2 ΔE units.

Acknowledgements

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References

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Author Biography

Clive E. Foster was born in Derby in 1971 and studied from 1990-1996 at Durham University, England. He obtained his PhD under the supervision of Professor David Parker. Following a year at the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr, Germany, with Professor Manfred T. Reetz, he took up his current position at Avecia. He currently works in the Ink Jet Printing Materials Research Group working on novel colorants for Ink Jet Applications.