The Problem of Catalytic Fading with Ink-Jet Inks

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Abstract

A challenge in formulating dye-based ink-jet inks that exhibit improved lightfastness is a phenomenon known as catalytic fading. This commonly refers to the fact that a given dye may fade faster when it is in contact with another dye as a result of an image area containing more than just one of the inks.

However, components in the ink and the media can also act as photocatalysts. For example, hydrogen donors initiate reduction of azo dyes, and singlet oxygen oxidizes them. An explanation is that the absorption of radiation in the UV or visible range can raise one of the dyes or ink components to an excited state. This can then either initiate reactions leading to degradation, or the energy is transferred to another dye whose excited state is at a lower level. In such an excited state, the dye becomes more reactive and is prone to degradation if it cannot quickly dissipate this excess energy away. Hammet constants and molecular modeling were found to be useful tools for correlating fading data.

If the source of the excitation is UV radiation, then UV absorbers can be incorporated into the formulation, or the image can be coated with an UV protective laminate that would also guard against any humidity effects. However, when the source is absorption of visible light which is what generates the color, then the problem becomes somewhat more complex. Quenchers can be added which serve as acceptors of the energy from the dye's excited state. Aggregation of the dye can also minimize the effect such that it is more pigment-like.

Introduction

Dyes generally resist fading in vacuo, but upon contact with the atmosphere, the media and other components in the ink they will fade to varying degrees. Unfortunately, our understanding of the controlling mechanisms is somewhat limited, and the approach to formulating ink-jet inks with lightfastness characteristics sufficient for archival purposes has been more of an empirical nature. However, the problem of photocatalytic fading has been under investigation for some time for other systems such as dyeing of textiles and polymers, and the fading mechanisms identified in these studies are useful in providing guidance to improve the lightfastness of ink-jet inks. Thus, we shall review those mechanisms that appear to be pertinent for ink-jet inks and discuss those parameters and guidelines which have been helpful in developing correlations with dye structure and in leading us to new products.

Fading of Azo Dyes

Reductive Mechanism

Two pathways by which azo dyes can fade are photoreduction and photooxidation reactions, and these are dependent on the dye's chemical environment as determined by the media, components in the ink and surrounding atmosphere. Under anaerobic conditions, an azo dye can be reduced to its corresponding amines by abstracting a hydrogen atom from a hydrogen donor as shown in Figure 1[1].

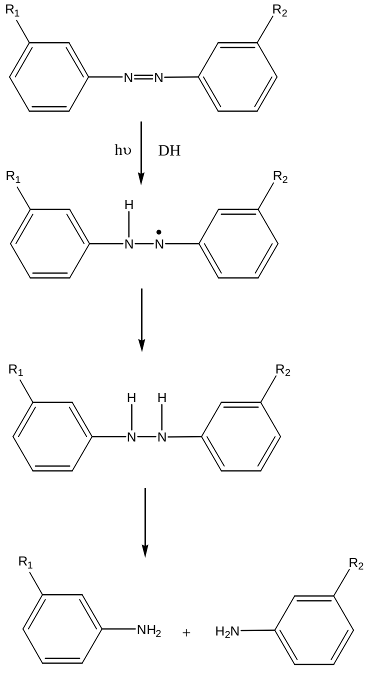


Figure 1. Reduction mechanism for azo dyes

This reaction set is greatly accelerated when either the hydrogen donor or dye is photo-excited, and its action spectrum is then determined by the absorption spectrum of the photoactive compound. Some examples of hydrogen donors are alcohols, amines, ketones, carboxylic acids, ethers and esters, and these absorb in the ultraviolet range. That this is indeed the action spectrum has been confirmed experimentally by van Beek and Heertjes [2]. In fact, the wavelength of active light varied only with the hydrogen donor and did not change for different azo dyes using paper soaked with their aqueous solutions and air dried.

Azo vs. Hydrazone Tautomers

Mallet and Newbold [3] have also found that there is a linear correlation of positive slope between the fading rate under nitrogen and the ratio of the hydrazone and azo tautomers in hydroxyazo dyes. The media was polypropylene which produces hydrogen radicals upon UV irradiation. This further supports the above reductive mechanism in that hydrazones are already in a partially reduced form.

The position and nature of substituents play a role in determining the state of the tautomeric equilibrium [4]. Since the azo group (N=N) is an electron acceptor, electron donating substituents, especially OCH_3, stabilize the azo tautomer. However, the imino group (NH) is an electron donor, and the hydrazone tautomer is favored by electron withdrawing substituents, especially NO_2.

Intramolecular hydrogen bonding can also provide additional stability to the hydrazone tautomer with certain structures [5]. Typically, this occurs between an OH group at the ortho position and the further nitrogen of the azo group. Since oxygen is more electronegative than nitrogen, it forms a stronger hydrogen bond, and thus the hydrazone tautomer is stabilized more.

Intermolecular hydrogen bonding with the media and components in the ink can have similar effects, and generally the more polar materials favor the hydrazone tautomer. Of course, the media restricts free tautomeric interchange.

Oxidative Mechanism

On the other hand, the oxidative fading of azo dyes has been attributed to the attack of singlet oxygen on their hydrazone tautomer as shown in Figure 2 [6]. The initial Ene reaction leads to the formation of an unstable peroxide which then undergoes decomposition. This reaction is promoted by singlet oxygen sensitisers such as anthraquinone dyes which upon excitation transfer their energy to the oxygen. Conversely, singlet oxygen quenchers such as 1,4-diazabicyclo[2,2,2]-octane (DABCO) and nickel-dibutyldithiocarbamate (NBC) suppress the fading. Such materials are not very water-soluble and are more easily incorporated into the media than the ink.

Effect of Substituents

The photochemical activity of both the reductive and oxidative mechanisms is also a function of the substituents in both the dye and hydrogen donor. Many studies have shown that a linear correlation exists between the logarithm of the fading rate and the Hammett constant of the substituent [6]. The Hammett equation is defined as [7]

$$\log (k/k_0) = \rho\, \sigma \qquad (1)$$

where k_0 is the rate or equilibrium constant for the reference hydrogen substituent, and k is the corresponding value for the R group in question.

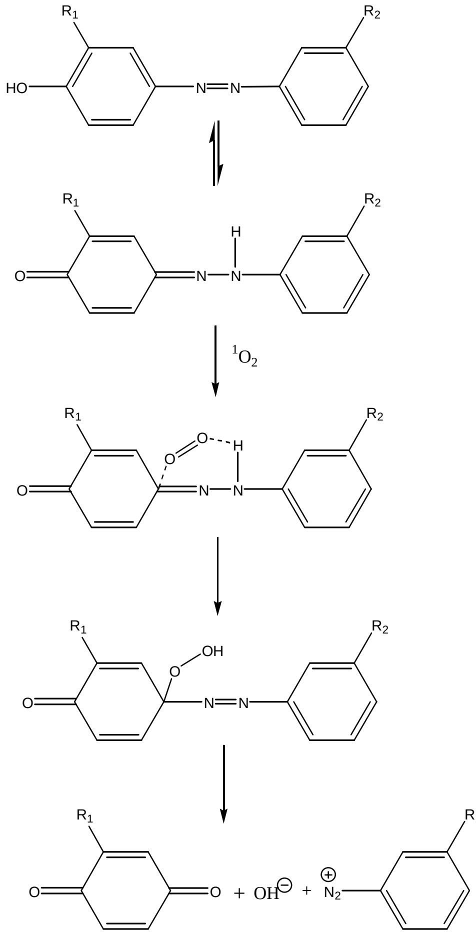


Figure 2. Oxidation mechanism for azo dyes.

The Hammett constant σ characterizes the electron withdrawing or donating strength of group R, and its tabulated values are based on dissociation data for substituted benzoic acids. The constant ρ measures the sensitivity of the reaction in question to electrical effects and is influenced by conditions such as temperature and its surroundings.

Figure 3 illustrates a typical plot of the fading rate against the Hammett constant. Since hydrogen is abstracted by electrophiles which are deficient in electrons, it is reasoned that the fading rate should increase with the more electron withdrawing substituents relative to hydrogen and thus increasingly positive values of the Hammett constant when reduction is the controlling mechanism.

Conversely, singlet oxygen is electrophilic and attacks positions of high electron density which is promoted by electron releasing substituents with negative Hammett constants in the case of oxidation. This is why metallized dyes with their electron withdrawing metal atom are particularly stable. Under moist conditions, singlet oxygen can also react with water to form hydrogen peroxide, and antioxidants can be used to decompose it.

Thus, correlations with either positive or negative slope can be obtained, and if both mechanisms are operating, a transition from one to the other will occur. In fact, the two individual rates could compensate for each other, resulting in little variation in the overall fading rate. Performing experiments under nitrogen and oxygen is helpful in sorting out such effects.

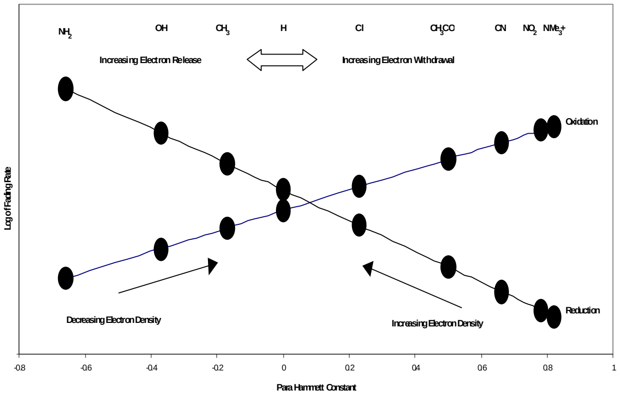
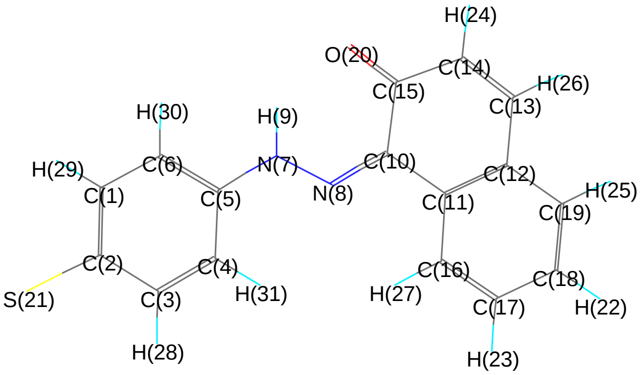


Figure 3. Schematic plot of the logarithm of fading rate vs. the Hammett constant

Table 1. Partial charges on selected atoms for substituted 1-phenylazo-2-naphthols.

Substituent	Hammett Constant	Q on N7	Q on N8	Q on H9	Q on C5	Q on C10	Q on O20	Log of Relative Fading Rate [8]
OCH_3	-0.28	0.06377	-0.16755	0.21201	-0.13609	-0.02855	-0.48313	0.21
CH_3	-0.14	0.02145	-0.17632	0.22917	-0.04291	-0.00172	-0.48444	0.12
H	0.00	-0.02654	-0.16387	0.24462	0.00623	0.00602	-0.48561	0.00
Cl	0.24	-0.05280	-0.16284	0.24835	0.07044	0.02304	-0.48030	-0.27
NO_2	0.81	-0.01142	-0.19208	0.23235	0.03505	0.05749	-0.46743	-0.82



While these correlations with the Hammett constant provide further support for the validity of these fading mechanisms, they do have their limitations. For example, only the substituent can be varied with the dye's structure held constant, and substituents in the ortho position generally do not correlate well. Since the partial charges on the atoms are what are really being varied, they can be calculated using molecular models. Fortunately, personal computers are now sufficiently powerful to handle such calculations for dye molecules. Using CambridgeSoft Chem3D, we carried out such calculations for substituted 1-phenylazo-2-naphthols as shown in Table 1. The structures were energy minimized by MOPAC using the AM1 potential function, and the Wang-Ford charge option was selected. Fading data under oxidative conditions is also included for comparison.

It is seen that the partial charge on carbon atom 10 where the Ene reaction takes place best follows the fading rate, and this plot is shown in Figure 4. As its charge decreases and thus its electron density increases, this reaction is encouraged, resulting in faster fading.

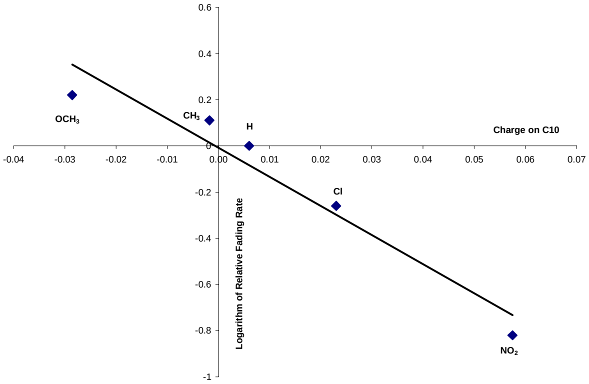


Figure 4. Fading rate vs. partial charge on carbon atom 10 for substituted 1-phenylazo-2-naphthols

Dyes as Photocatalysts

A troublesome problem encountered while developing our lightfast set of ink-jet inks was that certain dye combinations exhibited less stability when together in a print area in comparison to being separately printed. As mentioned earlier, excited dyes can produce singlet oxygen resulting in oxidative fading, but they can also transfer their absorbed energy to another dye at a lower energy level to increase its radiative exposure and fading.

One way to combat this situation is to add a quencher that takes on this energy and dissipates it harmlessly. Ideally, it functions by forming a complex with the dye that undergoes charge transfer and emission of the excess energy. The molecular orbital scheme in Figure 5 illustrates this process for the excited dye acting as an electron acceptor or donor, and the resulting free energy change that we wish to be negative is [9]

$$\Delta F = -{}^{1}\Delta E_A + IP_D - EA_A - C \qquad (2)$$

where ${}^{1}\Delta E_A$ is the singlet excitation energy of the electron acceptor and C is the coulombic energy gained. In arriving at this equation, the energy of the highest occupied molecular orbital Φ_{HOMO} was set equal to the ionization potential of the electron donor IP_D and the energy of the lowest unoccupied orbital Φ_{LUMO} to the electron affinity of the electron acceptor EA_A. Since electron affinities are in general not accurately known, they may be approximated by polarographic reduction potentials and ionization potentials by oxidation potentials. Φ_{HOMO} and Φ_{LUMO} may also be calculated using Chem3D.

This equation has been evaluated in several studies on fluorescence quenching and was found to have validity. For example, amines as electron donors became more effective quenchers for rubicene as their ionization potential decreased [10]. In contrast, a series of electron accepting quenchers became more effective for anthracene and pyrene as the electron affinity increased [10]. For a given electron donating quencher, Young and Martin [11] and Solomon et al. [12] both showed that quenching correlated with the sum of the electron affinity and excitation energy for a set of aromatic materials. Thus, each part of the equation has been checked out.

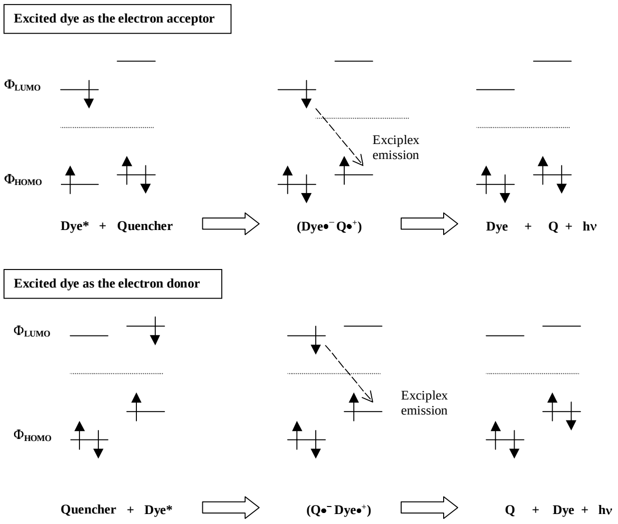


Figure 5. Exciplex formation via charge transfer.

Formulation Guidelines

There are a number of guidelines that can be drawn from this work to assist in minimizing the fading of ink-jet inks.

- Carry out fading experiments under both a nitrogen and oxygen atmosphere to help identify the contribution of the reduction and oxidation mechanisms. Doing this at different wavelengths is a plus. Select appropriate UV absorbers, accordingly. Check the composite black and primary color images for dye catalyzed fading and the need of a quencher.
- Avoid the presence of hydrogen donors and singlet oxygen sensitizers. Make use of substituents and the tautomers of azo dyes to minimize such interactions.
- As a general rule, dye aggregation reduces fading and is promoted by higher concentrations and certain surfactants.

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Biography

Dr. Walter J. Wnek is Chief Technical Officer for American Ink Jet Corp. and is responsible for the technical activities of the company leading to the development and manufacturing of ink-jet inks. He has 20 years of experience in the electronic imaging industry with both toners and ink-jet inks. Walter holds a Ph.D. degree in Chemical Engineering from the Illinois Institute of Technology and specializes in Colloid Science and the dispersion of colorants in polymers and liquids. He has published over 30 papers and given numerous presentations at various conferences on electronic imaging and related topics.