Properties of Inks Containing Novel Lightfastness Additives

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Abstract

Early ink jet inks were noted for their brilliance and other highly desirable color properties. However, dyes used to obtain these desirable properties are, almost without exception, susceptible to light-induced fading. Others' efforts to make advancements in dye fade resistance focused on modifying the structure of the dye chromophore; however, this modification has led to a reduction of favorable color properties. Kimberly-Clark has developed an additive system that will allow the use of dyes with the best possible color properties, while also providing protection against light-induced color fading. Lightfastness and color properties of ink formulations produced by Formulabs using these novel additives will be presented.

Introduction

Dyes used for ink jet printing inks have been studied intensely since the introduction of the ink jet printer. These dyes have been taken primarily from the class of soluble or disperse dyes used in textile applications. This subject will not be covered in depth here, however, review articles on the topic are available. [1-4] The driver for this intense study has been primarily a search for an increase in lightfastness and waterfastness of these dyes, and an increase in the color properties of these dyes. Changes in molecular structure in order to obtain better lightfastness is often associated with unwanted changes in color properties, primarily gamut volume. [5]

Light induced fading of dyes can occur by several mechanisms. Dyes, like other materials, can absorb photons which, either directly or indirectly, can cause or lead to the loss of color of the dye (dye decoloration). This paper will describe a system that will prevent, to varying degrees, light induced fading of dyes used in ink jet printing by intervening in many of the causative mechanisms and at the same time not cause substantial gamut change.

Light Induced Fading of Dyes

The light induced fading of dyes has been studied for some time. [6,7] Dyes, as a superclass, have many varied structural properties. Conjugated aromatic systems with quite varied substituents; diazo, triazo and tetraazo systems with conjugated substituents; and even substituted phthalocyanine systems have been used in ink jet printing. Therefore, it should not be surprising that the same mechanism is not equally important with each dye type. Nor should it be surprising that one single remedy, implemented by itself, is not enough to prevent dye fading in the general sense.

Photolysis

Photolysis is a process whereby a photon absorbed by

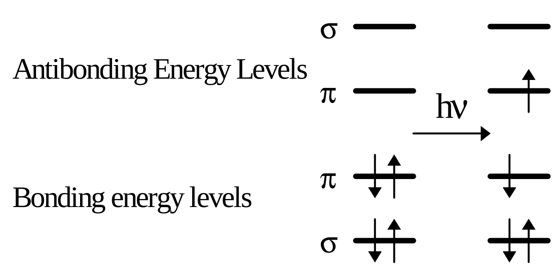

Figure 1: Pi Electron Excited by Photon.

the dye causes a lysis or breaking of a chemical bond forming two new species. The energy from the photon raises an electron from its ground state to an excited system. The bond from which this newly excited electron came can be broken. This lysis can be heterolytic - both electrons in the bond pair remaining with one of the new species - or homolytic - one electron remaining with each of the new species. The electron that absorbs the energy from the photon usually is a part of a pi bond (or multiple bond) system. Photolysis at this bond causes the system to loose the extent of conjugation necessary for the chromophore to appear as it did before the photon was absorbed. After this specific event, the molecule that absorbed the proton no longer is colored. The ink solution is now one molecule less in color density!

Role of Oxygen

Oxygen, or lack thereof, can play a major role in the outcome of an event where a dye molecule has adsorbed a photon. For example, an excited dye molecule - one that has adsorbed a photon but has not yet undergone photolysis or other relaxation routes - can react with ground state oxygen (oxygen is in the triplet state when at ground state) to become excited to the singlet state. Singlet oxygen is a powerful oxidant. Since the energy transfer event that caused the oxygen to become excited to the singlet state happened in close proximity of the dye (the excited dye was the culprit), the dye itself is the most likely target for singlet oxygen attack from a proximity point of view. Singlet oxygen is notorious for reacting with double bonds and other moieties that are responsible for the dye's color properties.

Role of Other Materials

Inks are always used on a substrate. This substrate is usually very white. When the substrate is paper, oftentimes optical brighteners have been used to make the paper appear as white as possible. These brighteners are designed to absorb photons of one energy - usually in the ultraviolet - and emit a photon of a lower energy in the visible spectrum. In effect, these brighteners are additional centers where photochemical reactions can begin and cascade. As the dye comes in contact with the brightener, the dye now has the opportunity to absorb energy, not from a photon, but from an optical brightener molecule that has been excited by absorbing a photon. These energy transfer mechanisms are well known, but are dependent on the energy levels within each of the two molecules. In short, some brighteners are more prone to cause this damage than others.

Some grades of paper are treated with strong oxidants in order to whiten the paper as much as possible. Traces of the oxidant itself, or other molecules that have been oxidized by the original oxidant can remain. These materials can cause degradation of the dye, or can participate in a photochemical chain of events, as in the case of the optical brightener leading to the eventual destruction of dye molecules.

Ink jet papers often use ink jet receiver coatings that are specifically tailored to increase print performance characteristics such as image quality. These coatings often consist of film forming polymers, polymers or other components used to manage the ink solvent (usually water, but sometimes glycols, etc.), components used to improve image quality, drying time, and a host of other print related variables. Binders and surfactants are also used to ensure that the coating formulation is easily placed onto and remains stable on the base sheet. Any one of these components can affect lightfastness. As an example, lightfast performance has been shown to be related to binder type. [7]

Interrupting Light Induced Fading Processes

Designing molecules to interrupt light induced fading processes is not trivial. There are a number of points at which the process can be interrupted. UV blockers have been used in dyes and paper coatings in order to significantly reduce the number of UV photons bombarding the dye. However, this is not altogether successful. Because the dye exhibits a significant absorption in the visible spectra, i.e., we can see the dye, it means that visible light can also be a culprit in the photochemical processes outlined above. Since blocking visible light is not an alternative, we must resign ourselves to the fact that the dye will be excited. The answer lies in how we handle the excited state of the dye. For example, the excited state of the dye can go through one of several relaxation pathways that do not result in the dye chromophore being destroyed. Additives can be used that directly interfere with the destructive pathway and cause a constructive pathway to be created. Additives based on this concept are the subject of patents that have recently been filed by Kimberly-Clark. These patent applications are currently being prosecuted and therefore will not be discussed here. However, results obtained when these types of additives were used will be presented.

Additive to Magenta and Yellow Inks

Cyan inks can be formulated using certain cyan dyes that are inherently lightfast. Phthalocyanine dyes fit into this category. For example cyan inks formulated using Acid Blue 199 often show excellent lightfastness. However, magenta and yellow inks formulated to take advantage of broad color gamut and other desirable color properties of certain magenta and yellow dyes often show a significant light induced fading. When an additive specifically tailored to reduce light fading in the magenta and yellow dyes was used, the lightfastness was increased while the color properties remained relatively unchanged.

A magenta ink was formulated using a basic ink vehicle formula and a mixture of Acid Red 52 and Reactive Red 181. While Acid Red 52 has excellent color properties, it also has the worst fading properties of magenta dyes used for ink jet inks.[8] The formulation contained appropriate surfactants, viscosity modifiers and other ingredients that were required in order to ensure that the ink was printable using a thermal drop-on-demand type printer. Using the same vehicle and the same magenta dyes, a second ink was formulated with the lightfast additive at a 0.5% loading. The additive was slightly colored therefore the dye mixture was adjusted to get the best match with the base formulation. Each formulation was then printed onto two paper types using an Encad Novajet III and let dry for two hours. The prints were then exposed to accelerated light induced fading conditions using an Atlas Weatherometer.[9] The fading cycle was 24 h with lights on, for four consecutive days, to total 96 hours of exposure. No dark time was permitted, water cycles were not used. The degree of fading and other color properties were measured and displayed in a uniform color space (L*,a*,b*). Differences in color fastness are reported as ΔE, or the vector change in color space (L*, a*, b*); and ΔH, or the vector change in the hue portion of the color space (a*, b*). All color measurements were made using an X-Rite Spectrodensitometer.

A yellow ink was formulated using Acid Yellow 17 dye and the same ink vehicle as outlined above. The ink was printed on two substrate types using an Encad Novajet III and faded under accelerated conditions in an Atlas Weatherometer. The fading and color properties were measured as in the magenta example. The results of the magenta and yellow fading are shown in Table 1 below.

Table 1. Fading of Inks With and Without Additives

	M Alone		M With Additive		Y Alone		Y With Additive	
	ΔE	ΔH	ΔE	ΔH	ΔE	ΔH	ΔE	ΔH
IJ Bond	44	10	12	4	29	5	8	3
Photogloss	65	17	20	6	48	7	15	4

Additive to Coated Paper Substrate

A photobase paper was coated with an ink jet receiver coating prepared using a typical formulation of a binder, surfactant and viscosity builder. The final coat weight was 10% and the binder portion was 70%. The photobase was also coated with the same vehicle where a portion (65%) of the binder was replaced with a light stabilizing additive. The hand sheets were then printed with a Novajet III and faded under accelerated conditions in an Atlas Weatherometer. The fading and color properties were measured as in the ink examples above. The fading results are shown below in Table 2.

Table 2. Fading of Inks on Photoglossy Papers

	M Alone		M With Additive		Y Alone		Y With Additive	
	ΔE	ΔH	ΔE	ΔH	ΔE	ΔH	ΔE	ΔH
PG	65	17	20	6	48	7	15	4
PG^+	20	8	4	1	16	4	3	1

PG: Photoglossy; PG^+: Photoglossy and Additive

A commercially available cyan ink was used with the magenta and yellow inks from above to make an ink set for the purpose of measuring color gamut volume. The color data obtained from the experiments above was combined with color data obtained from the cyan, two color patches (R, G, B), and a composite black produced using each of the inks produced above. The gamut volume of each ink set, i.e., one using unmodified Y and M inks and one using Y and M inks with lightfast additives, was calculated using the color data obtained from the fading studies above. Only the data from the unfaded inks were used, since comparison of inks faded to various degrees is not meaningful. These calculations indicate that the gamut volume can be maintained when a lightfast additive is used in the ink, or can be increased when a lightfast additive is used in the media. These calculations are summarized below in Table 3.

Table 3. Gamut Volume Calculations

	Inkset	Inkset with Additives
Photogloss	319,428	318,920
Photogloss with Additives	407,825	408,002

Discussion

The fading cycle used for these experiments is approximately equal to one month of outdoor exposure or five years of indoor exposure. Under these conditions, the ink and media additives show a significant decrease in light induced fading. Further, while the improvement with either the ink additive or the media additive alone is impressive, the improvement with both additives is startling. Since these effects were synergistic, or at a minimum additive, it is likely that these additives are not affecting the same type of protection from a photochemistry point of view.

Conclusions

Dyes used to make ink jet inks can be stabilized against light induced fading using additives in either the ink or the media. However, a much greater effect can be brought about by introducing lightfast additives into both the media and the ink. This protection can be afforded while maintaining or improving the color properties of the ink.

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