

Stabilization of Dye Based Images on Porous Media

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Abstract

Additives are identified that greatly reduce the fade of dye-based images on porous media. A series of additives were topically applied to commercial porous media that was then printed on with commercial dye-based ink sets. Significant differences in dye fade were observed upon simple ambient exposure under office lighting conditions. Non-yellowing compounds were identified which significantly slowed the rate of color loss of the prints, provided even fade over all colors screened, and introduced no discoloration on unprinted media surfaces.

Introduction

The introduction of micro- and nanoporous media for photo realistic ink jet printing presents new challenges for image permanence, especially for prints made with dye-based inks. Of particular concern is the issue of 'gas fade', i. e., the loss of color due to the presence of atmospheric pollutants and the impact this has on the use of accelerated test methods in predicting the service lifetime of such prints.

Dye fade is a complex phenomenon involving a number of variables, e. g., light, moisture, pH, airborne pollutants, media interactions, etc. Nonetheless, significant improvements in the permanence of dyes in dense polymer media have been made by using data from accelerated tests that attempt to examine individual components of fade separately, as in the use of high intensity light to increase the observed rate of photo degradation. These tests, however, are only valid if they can be correlated with real time aging. Results from an accelerated test should match the relative differences noted in actual unaccelerated use. Without this reciprocity, differences noted in the lab cannot be converted to improvements in actual service in the field.

A certain degree of reciprocity failure, the lack of correlation with real time aging, is encountered in most accelerated aging. In many cases, reciprocity failure is small enough so that the accelerated tests can be used with a degree of cautious confidence in understanding the causes of fade and developing solutions.

However, reciprocity failure has been significant in the accelerated photo aging of porous media images. In these systems, reactions involving atmospheric pollutants play a larger role in dye fade, typically competing with, or overwhelming, the rate of dye loss due to solar radiation.¹

Ozone has been implicated as the major cause of these reactions, many of which occur readily in the dark.

Many complications are encountered when studying the impact of gas fade of porous media images,² even using non-accelerated tests. For example, the concentration of pollutants such as ozone varies from season to season and place to place.³ High humidity levels also greatly enhance the rate of ozone degradation.

Furthermore, while ozone causes dye degradation via reactions that do not require light, the possibility remains that other airborne materials, such as SO₂ and NOX gasses can combine with light to accelerate dye loss. Singlet oxygen production may also be enhanced by the presence of inorganics found in the coating, or through interactions between the dye and the inorganic support.⁴

Image permanence can be improved by modification of dye structure, ink formulation, or media formulation. The use of over lacquers or protective laminates would reduce fade but add cost and extra processing. Pigments are less prone to fade but present other complications such as ink dispersion stability and differential gloss. The ultimate solution most likely will require the combination more than one of these alternatives.

The use of stabilizing additives would seem to be an attractive part of the solution. While light stabilizers and antioxidants greatly extend the service lifetime of many polymeric systems, there are significant challenges in their use in stabilizing dyes. These include maintaining close contact between the additive and dye, and finding an additive that functions for more than one class of dye given the probability of multiple degradation mechanisms.

We have investigated the possibility of preventing the excessive fade on porous media with additives. While not optimized, we have found that real improvements in dye fade can be obtained by incorporation of suitable stabilizers. As expected, some additives work better on one class of dye than others; however, we have found compounds that are effective for several different dye chemistries. This is important not only for its commercial potential, but also for what it may tell us about the mechanisms of dye loss.

Experimental

Test patterns consisting of single colored one inch square blocks of cyan, magenta, and yellow, or cyan, magenta, yellow, and black at 100% and 50% print density were

printed using commercially available printers and dye-based ink sets on commercially available media. Prints were dried 24 hours prior to initial color measurements.

CIEL*a*b* color (delta E) and optical density (delta T) were measured using a X-Rite Spectrodensitometer using a white tile blank. Aging was carried out under ambient office conditions.

Application of Additive to Media Surface

Approximately 5 grams of a 0.4% by weight solution of the additive in methanol was sprayed onto a 0.06 m² sheet of commercial photo glossy nanoporous media using a flask type chromatography sprayer. A blank was prepared by spraying the same quantity of neat methanol on the paper. The paper was allowed to dry at least 24 hours. The final concentration of additive was 650-700 mg/m².

Results

Comparison of Image Aging / Storage Conditions

Initially, a selection of commercial photo realistic papers was obtained, six SiO₂-based porous papers and four dense polymer papers predominately either PVOH or gelatin. A three-color test pattern was printed on each (HP 970). A sample of each print was then stored in the following office environments with 24 hour fluorescent lighting:

- desk top
- in a desk drawer
- in a polyethylene bag, desk top
- in a polyethylene bag, desk drawer.

Figures 1a and 1b shows the average change in color (delta E) for cyan and magenta after four weeks. There was little yellow fade throughout this work and will be omitted from discussion.

While absolute amount of fade differed for individual papers, it was immediately clear that the SiO₂ based porous media suffered greater dye fade in most environments. Note also that the dense media prints exhibit similar light induced fade for either bagged or unbagged samples, whereas the porous media prints exhibit greater fade, dark or light exposure when the print is exposed to air, i.e., unbagged.

The extreme fade seen for the desk top exposures without a bag may be due to the combined effects of light and air, or may simply be due to greater air flow relative to the inside of a drawer. The data, however, clearly shows that light causes measurable color change for porous prints, as seen in the polyethylene bag exposures, and some interaction between light and pollutants, or even light and oxygen, cannot be ruled out.

Additive Screening

Given the rapid dye fade seen for the nanoporous materials under non-accelerated, 'real world' conditions, and the possibility that the interaction of different factors, such as light, humidity, and other atmospheric conditions, would impact the rate of dye degradation, additives were

screened using ambient aging. Prints were placed on an office desk top under 24 hr/day fluorescent lighting.

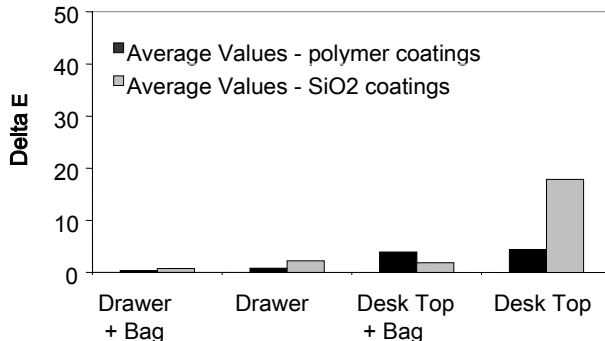


Figure 1a. Cyan fade from commercial paper after 4 weeks office exposure.

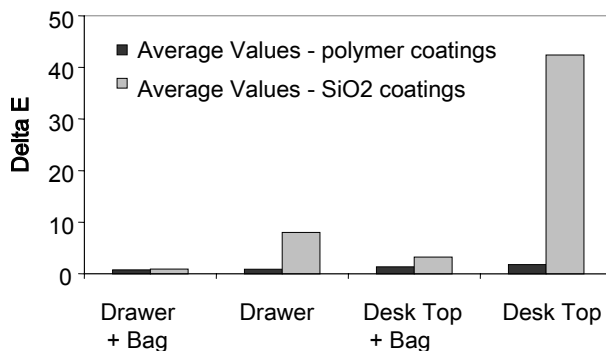


Figure 1b. Magenta fade from commercial paper after 4 weeks office exposure.

We chose to work mainly with papers that exhibited the most rapid dye loss. Additives were sprayed onto the papers as described in the Experimental section. It must be noted that we are using mismatched inks and media and a direct comparison of the absolute fade observed here with other systems cannot be made.

Dozens of compounds representing several different chemical classes were tested. Many compounds gave small improvements, but very few had much of an impact. For clarity this discussion will focus on just a few significant compounds, the previously disclosed phenol 1,⁵ nitroxyl 2,⁶ piperidyl hydroxylamine salts 3 and 4,⁵ see Fig. 2, and two novel compounds 5 and 6.

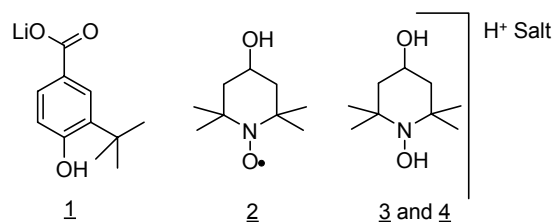


Figure 2. Previously disclosed structures.

HP 990

Figure 3a shows the cyan and magenta optical density loss from 100% print density patterns made with the HP 990 printer; Figure 3b shows the loss of the 50% print density squares. Again, there was very little loss of yellow. Also shown is the very small amount of fade for HP Photo Premium (Prm), a dense polymer paper.

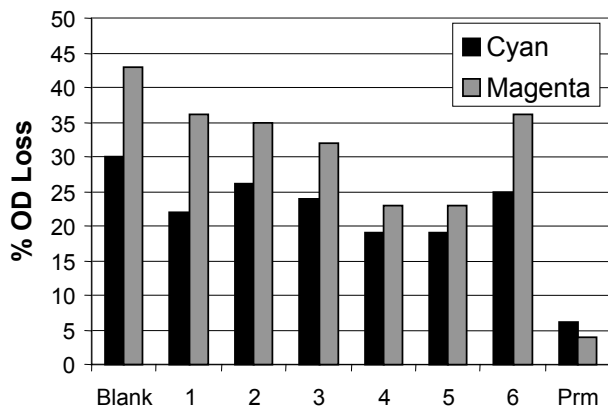


Figure 3a. Dye fade after 3 months office exposure, HP 990 printer, 100% print density.

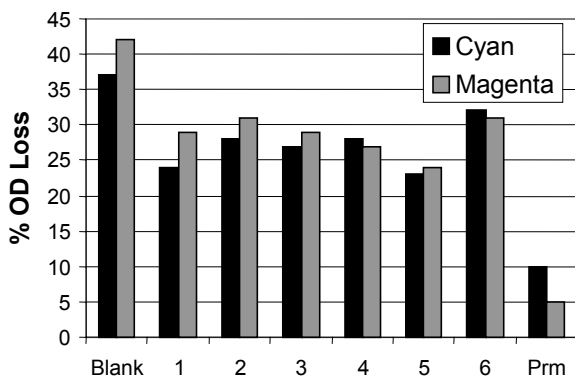


Figure 3b. Dye fade after 3 months office exposure, HP 990 printer, 50% print density.

The most effective compounds in this screen were the hindered piperidyl hydroxylamine salt 4 and the novel compound 5, with 5 being the best when comparing both 100% and 50% print density data. There was little change in 100% black, but in 50% black, 5 was again best at reducing fade. Also, compounds 5 and 6 have very similar structures, are in fact derivatives of each other, but the performance difference is striking and consistent throughout our work.

While the phenol 1 shows some activity, it can stain the paper and the discoloration may become noticeable upon aging. Such discoloration is a vital concern, and outside of 1 only the nitroxyl 2 exhibited modest staining.

It is also important that the additive not be sacrificial or prematurely degrade in use. Figure 4 tracks the OD loss over time for the 100% magenta square for the Blank, cmpd

1, and cmpd 5. The rate of dye fade for cmpd 5 continues to be slower after 3 months than the other two samples showing that the compound remains active and the effect is more than a short lived artifact of the printing process. Similar trends were seen with the other colors.

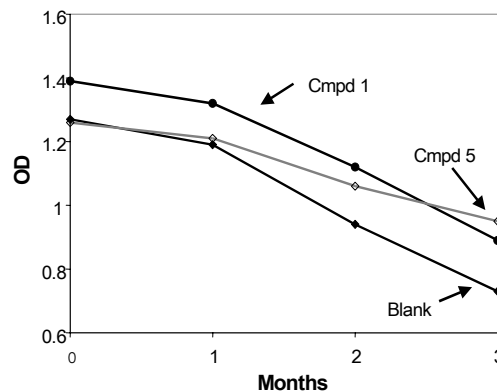


Figure 4. HP 990 Magenta Fade over time, 100% print density.

HP 5550

Similar results were obtained with prints made with the HP 5550 printer on the same paper. One notable difference was the profound fade in black with this printer. On all samples there was a tendency for the black to turn green, seen most vividly at 50% print density. Again, compound 5 offered the most overall improvement, although the black still trended noticeably green.

Paper B

Another paper with a different fade profile was also tested. Prints on Paper B, aged at the same time as above under the same conditions, exhibited much slower dye fade in the early months of the screen, but faded rapidly after three months. The change may be a characteristic of the paper formulation, or may represent a greater sensitivity of this paper to atmospheric changes as spring turned into summer. Again, compound 5 was effective, see figure 5.

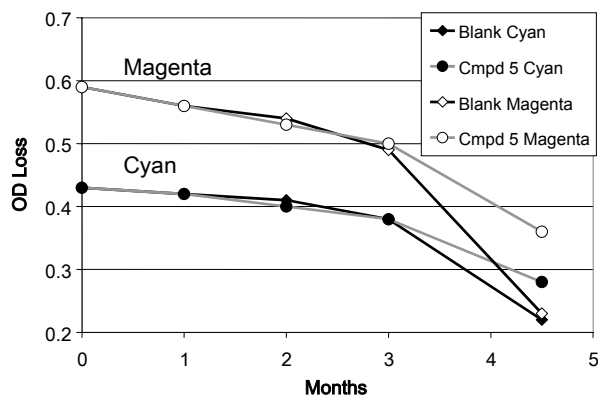


Figure 5. Dye fade from Paper B over time.

Discussion

Before further analysis of the results, a closer examination of the data presentation must be made. In earlier testing, good correlation was between delta E, optical density (OD), and visual inspection. In later work, OD measurements still correlated with visual inspection, but delta E readings began to show more scatter. Loss of OD is usually presented as a percentage of original OD. This is probably only valid when comparing samples that had similar starting densities. Also, in many earlier tests, differences in fade were more pronounced at earlier intervals. This could either represent changes made to the papers or inks over time, or a greater dependency on atmospheric conditions as our offices are no longer fully air-conditioned on weekends.

It is still worthy of note that in the earlier tests, where rapid early fade was observed and correlation between delta E and OD was good, the impact of some stabilizers, especially 5 appeared even greater, see Figure 6. This change in stabilizer performance may reflect some human error in formulation or some change in the paper or ink composition. However, it may also be that there are numerous dye fade pathways involving interactions of different factors that are more prevalent under different conditions, and the stabilizers employed work more efficiently on some than others.

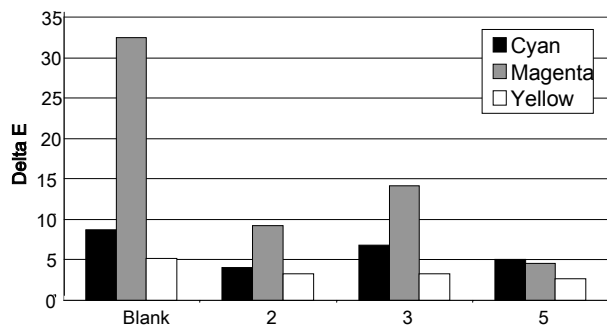


Figure 6. Dye fade in early test at 13 weeks, HP 970 printer, 100% print density

Dye fade is much greater for porous media than others.⁷ Certainly this can be attributed partly to the greater actual surface area of the dye exposed. The shape of the silica surface, with holes and crevices, spreads the dye thinner over a larger surface. This diminishes the prospect for dye aggregation, which is an important feature of stable dyes, and exposes more dye to harmful gasses such as ozone.

But the potential exists for other important degradation pathways. Tight silica/dye association makes electron transfer from the dye into a metal conduction band likely given the appropriate orbital energies.¹ The absorbance of UV light by all dyes, even cyan, would drive this process. The cation radical/anion radical produced could react with

oxygen or other destructive species or back electron transfer.

The back transfer can be non-destructive, but the electron transfer is not subject to the same selection rules as photo excitation and spin flip to form the dye triplet becomes more likely. This not only introduces the prospect of triplet chemistry, but also dye sensitization of singlet oxygen.⁸ It has also been shown that irradiation of silica gel at 350 nm can lead directly to singlet oxygen formation.⁹

It cannot be ascertained from the above work how the stabilizers are functioning. Given that some additives such as compd 5 are effective on different classes of dyes in preventing ambient fade, and regenerative non-coloring antiozonants are a rare species, it is tempting to suggest that the additive is interfering with a process that is fundamental to the fade of any dye in this environment. Interference with a process that is either caused by, or accelerated by the silica species is therefore favored as the mechanism by which the additive is acting.

Conclusion

Additives can play an important role in improving the permanence of dye-based images on nanoporous media under ambient conditions. It is unclear whether the additives which were found to be effective were preventing photo degradation or a more complicated mechanism involving light and some components of gas fade.

References

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Biography

Joseph Suhadolnik is Senior Staff Scientist in the Research department of Ciba Specialty Chemicals in Tarrytown, New York. Principal areas of research include the photochemistry of light stabilizers and photo-decomposition of dyes and pigments. He holds several patents on novel light stabilizers and has published papers on the degradation mechanisms of UVAs. He received a B.A. in chemistry from the University of Pennsylvania in 1980 and Ph.D. in organic chemistry from the University of Minnesota in 1985.