Effects of Molecular Substituents of Copper Phthalocyanine Dyes on Ozone Fading

Fariza B. Hasan, Michael P. Filosa and Zbigniew J. Hinz; ZINK Imaging LLC. Waltham, Massachusetts, USA

Abstract

Copper phthalocyanine dyes, widely used in various imaging systems, are susceptible to gas fading under ambient conditions. One of the main factors responsible for such fading is the presence of ozone. Addition of suitable antiozonants has been shown to be effective in improving ozone stability. Although the exact mechanism of such stabilization is not fully understood, the electronic structures of the additives have shown significant impact on their effectiveness. In order to increase the ozone stability of copper phthalocyanine dyes without any additives, several copper phthalocyanine dyes containing substituents of varying electronic structures were synthesized and tested for ozone stability. The structure of a copper phthalocyanine dye with significantly improved stability to ozone is described in this paper. Possible mechanisms leading to such stability are also discussed.

Introduction

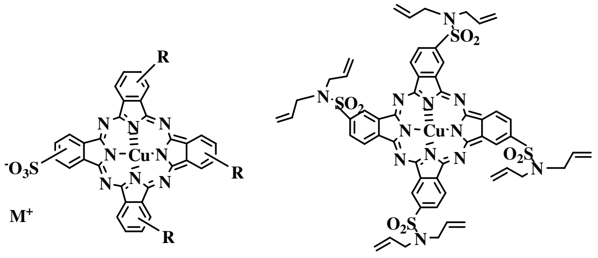
Copper phthalocyanine (CuPC) dyes are extensively used in various imaging systems because of several advantages, such as high spectral absorptivity, solubility in various common organic solvents and light fastness. However these dyes are also susceptible to ozone fading under various ambient conditions, which can cause deterioration of images. A large number of papers related to the effects of ozone exposure on image stability have been published. Some of the recent publications are referred to in this paper [1-11].

Several types of materials commonly used as antiozonants in other industries, such as p-phenylenediamines for reducing degradation of rubber due to exposure to ozone are not suitable for imaging systems, because of the highly colored products formed due to their reaction with ozone. These reactions have been shown to proceed through electron transfer mechanisms [12]. Organic phosphites act mainly as antioxidants but have low solubility in water or common organic solvents, and are not suitable for imaging systems. Other methods used for minimizing degradation of rubber due to exposure to ozone, such as coating with impermeable materials is not easily applicable to imaging products, except in a limited number of imaging systems where polymeric materials can be transferred over the printed images. However, in such systems the efficiency of these materials depends on the continuity of the transferred layer, and any defect present in this layer would allow ozone to diffuse through and cause degradation of the dye.

Several aminoanthraquinone dyes, which have similar functional groups as p-phenylenediamines are efficient antiozonants, but do not form highly colored reaction products, due to the presence of electron withdrawing carbonyl groups in the fused ring systems [13, 14]. Aminoanthraquinone dyes, as well as p-phenylenediamines are essentially ozone scavengers, and thus reduce the availability of ozone to react with CuPC dyes. It is expected that the presence of molecular substituents that can act as ozone scavengers would render the CuPC dye molecules more resistant to fading and discoloration due to exposure to ozone. In order to test this hypothesis, and since the reaction of olefins with ozone is well known, a CuPC dye with allyl substituents was synthesized. To confirm the mechanism, two other CuPC dyes with different substituents were also synthesized and tested.

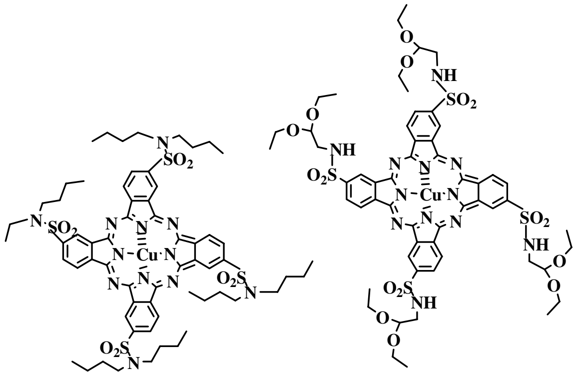
Substituted Copper Phthalocyanine Dyes

The structures of the CuPC dyes with varying substituents are shown in Figure 1. Although the exact structure of the commercially available CuPC dye, used as the control for the tests is not known, it is possibly a mixture of several isomers, containing various ring substituents, and represented as CuPC-A. The synthesized dyes are CuPC-B, CuPC-C and CuPC-D.



CuPC-A
Commercially available dye

CuPC-B
Diallyl substituted



CuPC-C
Dibutyl substituted

CuPC-D
Diethoxyacetal substituted

Figure 1. CuPC dyes

Experimental Procedure

For comparing the ozone stability of CuPC dyes containing various substituents, as well as the commercially available CuPC dye, images were generated by thermally transferring the dyes and a suitable thermal solvent from a donor to a porous receiver. The coverage of the dyes coated on donor sheets was maintained constant. The Dmax regions of the transferred images were exposed in an ozone chamber constructed from a Pyrex jar (1.2 ft^3) and a mercury-argon lamp [15]. Ozone was produced in situ, by the direct photolysis of oxygen in the ambient air within the chamber. A fan within the chamber ensured that all samples were uniformly exposed. The temperature in the ozone chamber was between 21-23^oC and relative humidity was 47-50%. The images were exposed to ozone for definite periods of time. For each set of experiments, a "control" image, which was an image of CuPC-A with cyan reflection density of very close to 1, was exposed with the tests samples. A comparison of the extent of change of each of these "control" coatings was used as a method to calibrate the effective ozone concentration in the chamber for each experiment. However, during the short period of time in which these experiments were conducted the changes of the "control" coatings were practically identical, indicating the concentration of ozone in the chamber during these experiments remained unchanged. Since the aim of these experiments was to compare the ozone resistance of the CuPC dyes under identical conditions, it was not necessary to measure the exact concentration of ozone in the chamber. The ozone stability of each of these dyes was compared by overall spectral changes and quantified by the extent of the initial reflection densities (cyan, magenta and yellow) and colorimetric parameters (L*, a* and b*) of the images before and after ozone exposure. A Gretag SPM500 densitometer was used for these measurements. The conditions for the measurements were: illumination = D50, observer angle = 2^o, density standard = ANSI A, reflection standard = white base, and no filter.

Results and Discussion

Figure 2 shows the reflection spectra of images of CuPC-A and CuPC-B, before and after exposure to ozone. The CuPC-A image showed large changes, including significant decrease of cyan density and increase of yellow density, but the CuPC-B image after exposure to ozone remained almost unchanged.

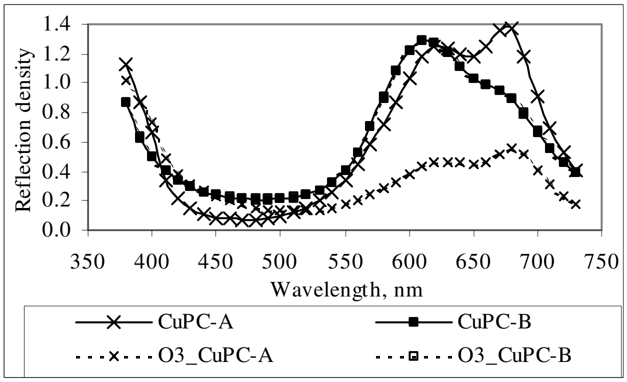


Figure 2. Effects of Ozone Exposure on Spectral Changes of CuPC-A and CuPC-B

In order to determine if the ozone stability of CuPC-B is due to the allyl groups, two other dyes, CuPC-C and CuPC-D, in which the allyl groups are replaced by butyl and ethoxyacetal groups respectively, were also synthesized and tested. The results, shown in Figures 3 and 4 indicate greater spectral changes for both CuPC-C and CuPC-D, compared to the changes for CuPC-B. However, both were more stable than CuPC-A.

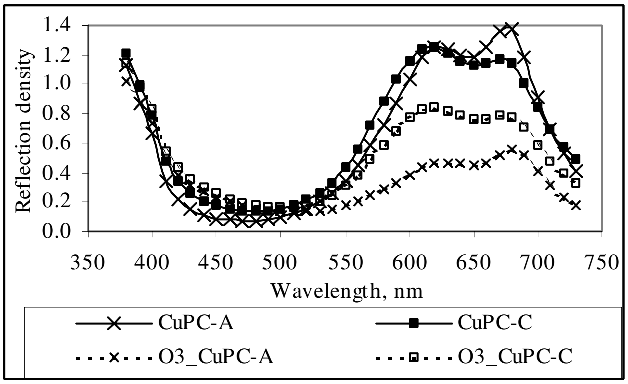


Figure 3. Effects of Ozone Exposure on Spectral Changes of CuPC-A and CuPC-C

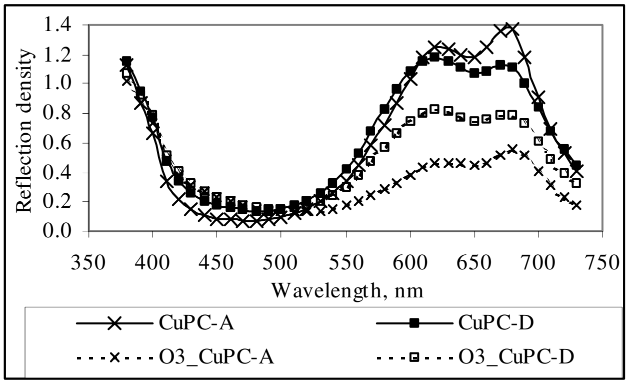


Figure 4. Effects of Ozone Exposure on Spectral Changes of CuPC-A and CuPC-D

The changes in cyan, magenta and yellow densities, and L*, a* and b* values of images from each of the four dyes after exposure to ozone are listed in Tables I and II, respectively.

The data indicate that the ozone stability of CuPC-B, containing allyl substituents, is considerably greater than that of the butyl or ethoxyacetal substituted CuPC. A comparison of the spectra of the four dyes shows that the presence of more H-aggregates, as indicated by the blue shift of the spectra, is associated with the observed ozone stability. The spectra of the dyes, dissolved in methylene chloride are practically identical and do not show such aggregation. It is possible that the allyl groups facilitate the required rearrangement of the molecules to cause such aggregation more than the other substituents. In addition, the allyl groups may react with ozone, and further protecting the chromophore.

Table I: Effects of ozone exposure on C, M, Y densities of printed images of CuPC dyes

		D[C]	D[M]	D[Y]
CuPC-A	Initial density	1.22	0.23	0.10
	Final density	0.46	0.15	0.26
	Ratio, final/initial	0.38	0.65	2.60
CuPC-B	Initial density	1.20	0.31	0.25
	Final density	1.19	0.31	0.26
	Ratio, final/initial	0.99	1.00	1.04
CuPC-C	Initial density	1.20	0.30	0.20
	Final density	0.82	0.24	0.28
	Ratio, final/initial	0.68	0.80	1.40
CuPC-D	Initial density	1.15	0.30	0.20
	Final density	0.80	0.23	0.26
	Ratio, final/initial	0.70	0.77	1.30

Table II: Effects of ozone exposure on L*, a* b* values of printed images of CuPC dyes

		L*	a*	b*
CuPC-A	Initial	68.82	-45.86	-38.88
	Final	81.12	-27.49	-1.29
	Change	12.30	18.37	37.59
CuPC-B	Initial	62.78	-46.42	-30.19
	Final	62.75	-46.43	-29.81
	Change	-0.03	-0.01	0.38
CuPC-C	Initial	63.73	-45.35	-36.36
	Final	70.45	-41.70	-16.59
	Change	6.72	3.65	19.77
CuPC-D	Initial	64.56	-44.71	-34.32
	Final	70.88	-40.31	-17.96
	Change	6.32	4.40	16.36

Conclusions

- Molecular substituents of copper phthalocyanine dyes show large effects on ozone fading of the printed images.
- Stability to exposure to ozone is increased, possibly due to chemical reaction of the molecular substituents with ozone, and the formation of aggregates that are more stable than the monomeric dyes.

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Author Biography

Fariza Hasan, currently employed at ZINK Imaging, LLC. in Massachusetts, received her Ph.D. in chemistry from University of British Columbia, Vancouver, Canada. Her graduate and post-doctoral research included kinetics and mechanisms of various organic, inorganic and biochemical reactions. The technical responsibilities in her current and previous positions consist of optimization and design of several existing and new silver halide and digital imaging systems. She has a total of approximately forty scientific publications and patents, and is a member of the IS&T and the American Chemical Society.