Journal of Imaging Science and Technology® 51(5): 419–423, 2007.

Effects of Molecular Substituents of Copper Phthalocyanine Dyes on Ozone Fading

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Abstract. *Copper phthalocyanine dyes, widely used in various imaging systems, are susceptible to 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 to have 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. © 2007 Society for Imaging Science and Technology.*
[DOI: 10.2352/J.ImagingSci.Technol.(2007)51:5(419)]

INTRODUCTION

Copper phthalocyanine (CuPC) dyes are extensively used in various imaging systems because of several advantages, including high spectral absorptivity, solubility in various common solvents, and relatively greater lightfastness compared to several other classes of dyes. However, CuPC 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 article.[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 reactions with ozone. These reactions have been shown to proceed through electron transfer mechanisms.[12] Other methods used for minimizing degradation of rubber due to exposure to ozone, such as coating with impermeable materials, are 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 polymeric layer, and any defect present in this layer would allow ozone to diffuse through and cause degradation of the dyes in images.

Several aminoanthraquinone dyes having similar functional groups as *p*-phenylenediamines are efficient antiozonants, but they 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, which can act as ozone scavengers would also 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 verify the mechanism, two other CuPC dyes with different substituents were also synthesized and tested.

EXPERIMENTAL PROCEDURES

Substituted Copper Phthalocyanine Dyes

The structures of the synthesized CuPC dyes with varying substituents, labeled as CuPC-B, CuPC-C, and CuPC-D, are shown in Figure 1. A commercially available CuPC dye, Solvent Blue 70 (CAS No. 12237-24-0) was used as the control for the tests. Although the exact structure of this dye is not known, it is possibly a mixture of several isomers containing various ring substituents, and can be represented as CuPC-A.

Synthesis of Copper Phthalocyanine Dyes

The synthetic method used for the substituted copper phthalocyanine dyes is described in Scheme 1.[15] Copper phthalocyaninetetrasulfonic acid tetrasodium salt (Aldrich), containing four $-SO_3Na$ groups as ring substituents was suspended in a 4:1 mixture of sulfolane and dimethylacetamide. A 32-fold excess of phosphorus oxychloride was added, and the reaction mixture was allowed to reflux for 4 h, after which the reaction mixture was cooled to room temperature and poured into rapidly stirring ice water. The blue precipitated solid was collected, washed with water, and dried in a vacuum desiccator at room temperature for 24 h. The crude wet cake, with some water present, was dissolved/suspended in methylene chloride and cooled to 4°C. A large excess of diallyl amine (for CuPC-B), dibutylamine (for CuPC-C) or diethoxyethylamine (for

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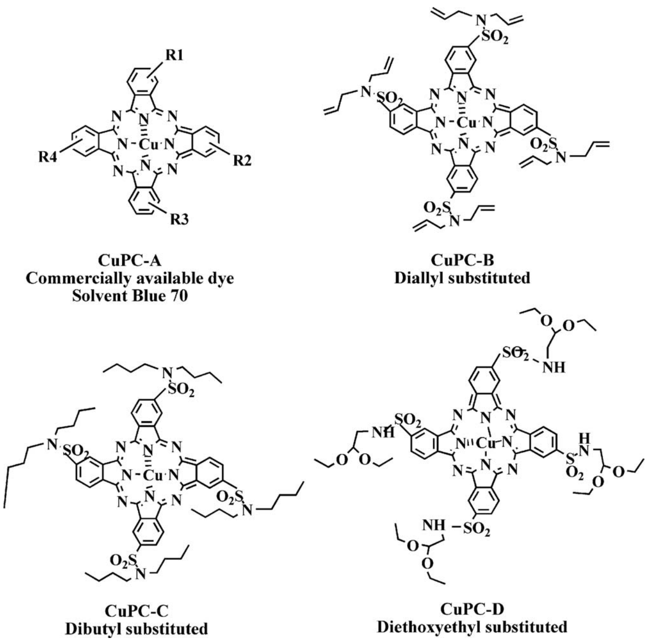
Received Jan. 11, 2007; accepted for publication Mar. 1, 2007.
1062-3701/2007/51(5)/419/5/$20.00.



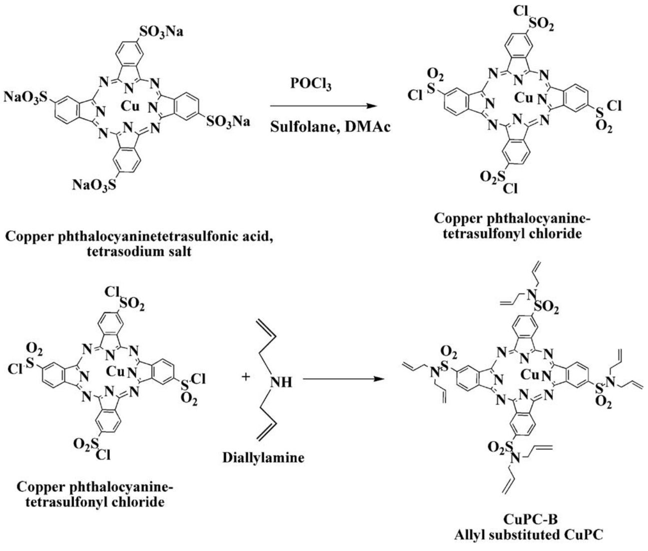
CuPC-A
Commercially available dye
Solvent Blue 70

CuPC-B
Diallyl substituted

CuPC-C
Dibutyl substituted

CuPC-D
Diethoxyethyl substituted

Figure 1. Structures of copper phthalocyanine dyes tested.



Copper phthalocyaninetetrasulfonic acid, tetrasodium salt

Copper phthalocyanine-tetrasulfonyl chloride

Copper phthalocyanine-tetrasulfonyl chloride

CuPC-B
Allyl substituted CuPC

Scheme 1.

CuPC-D) was slowly added to the cooled solution and then allowed to warm to room temperature and stirred for 16 h. The crude reaction mixture was placed onto a plug of dry of silica gel and eluted with methylene chloride. A greenish colored material came off and was discarded. The silica with the product adhering to it was sucked down until nearly dry. The elution was continued with a mixture of ethyl acetate/hexanes, 1:1 by volume. This process removed a dark brown impurity from the product. The eluent mixture was changed to one containing 4:1 ethyl acetate/hexanes. This fraction contained the desired copper phthalocyanine dye.

Imaging Method

Printed images of the dyes were generated by thermally transferring the coated dyes and suitable thermal solvents, without any polymeric binder from a donor sheet to a porous receiver.[16] The material used as donor sheets for these experiments was 4.5 μm thick PET with backcoat containing lubricant suitable for thermal printing. The receiver consisted of a coating of fumed silica with a hydrophilic polymeric binder system on a polyester base. The coverage of the dyes coated on donor sheets was maintained constant (285 mg/m^2). No protective coating was transferred over the images. Standard-type thermal printheads for monochrome prints were used for transferring the images, at maximum energy of 2.5 J/cm^2.

Spectra of Copper Phthalocyanine Dyes

Absorption spectra of the dyes in solution were obtained, after dissolving the dyes in methylene chloride, using a HP8452A diode array spectrophotometer. The reflection spectra of the dyes were measured at the $D_{\max}$ regions of printed images of the dyes, using a Gretag SPM500 densitometer. The conditions for the measurements were: illumination=D50, observer angle=2°, density standard=ANSI A, reflection standard=white base, and no filter.

Ozone Stability Test Method

To evaluate the ozone stability of the synthesized CuPC dyes containing various substituents, as well as the commercially available CuPC dye, the $D_{\max}$ 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.[17] 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 °C and 23 °C 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 the control commercially available dye, CuPC-A with cyan reflection density of very close to unity, was exposed for 1 h with the tests samples. A comparison of the extent of change of each of these "control" images 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 images were practically identical, which indicated that 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 changes of the reflection densities (cyan, magenta, and yellow) and colorimetric parameters (L^*, a^*, and b^*) of the images after ozone exposure, using a Gretag SPM500 densitometer. The conditions for the measurements are as described in the previous paragraph.

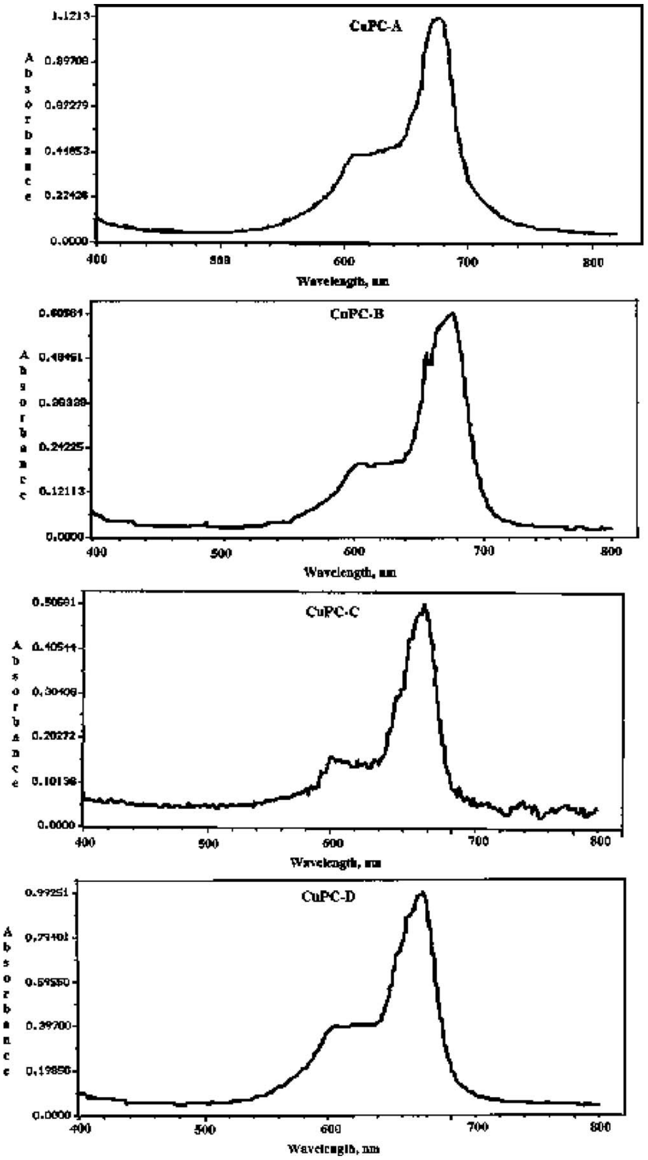


Figure 2. Comparison of spectra of CuPC dyes in methylene chloride solution.

RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of the commercially available and the three synthesized copper phthalocyanine dyes in methylene chloride. Although the solution spectra of these dyes are not identical, they are similar to each other. These results indicate that the electronic structures of the substituents have minor or insignificant effects on the chromophore. However, a comparison of the reflection spectra of the transferred images of the three dyes, shown in Figure 3, indicates significant differences between the spectra of the dyes. Although all three dyes show blueshifts of the transferred images compared to their spectra in solution, which is an indication of H-aggregation, CuPC-B shows greater shift than the other two synthesized dyes. It is likely that the planar allyl groups facilitate the stacking of the dye molecules more than the nonplanar butyl and diethoxyethyl groups, causing such aggregation.

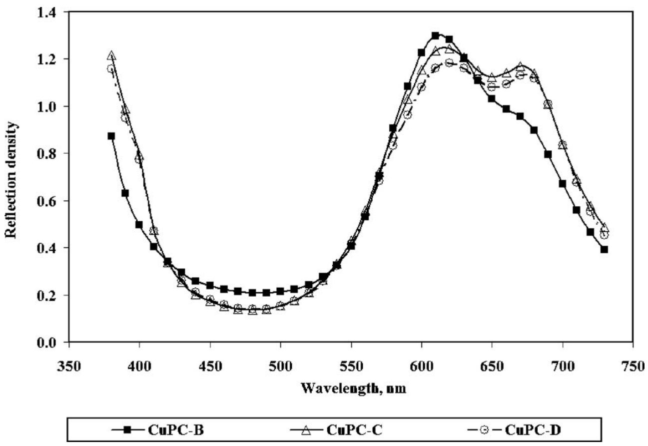


Figure 3. Comparison of spectra of thermally transferred images of CuPC dyes.

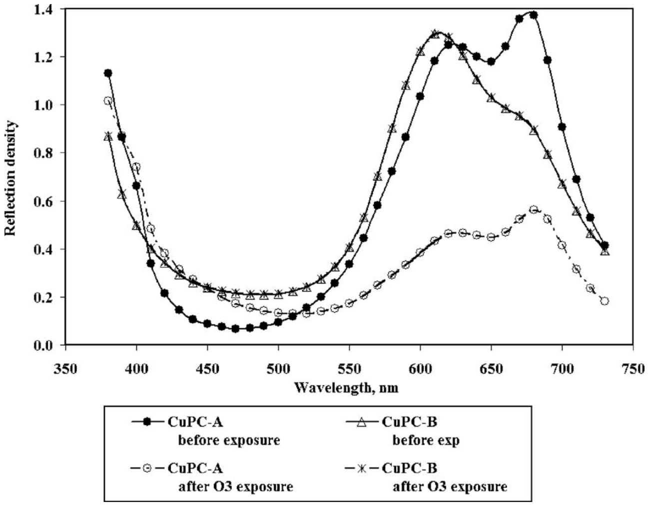


Figure 4. Ozone induced spectral changes on thermally transferred images of CuPC-A and CuPC-B.

Figure 4 shows the reflection spectra of images of CuPC-A and CuPC-B, before and after exposure to ozone for 1 h. The control CuPC-A image showed large changes, including a significant decrease of cyan density and increase of yellow density, which is due to the chemical degradation of the chromophore by ozone. The CuPC-B image after exposure to ozone under identical conditions remained almost unchanged. In order to determine if the observed ozone stability of CuPC-B is due to the steric hindrance caused by the allyl groups on the reaction of ozone with the chromophore, two other dyes, CuPC-C and CuPC-D, in which the allyl groups were replaced by butyl and diethoxyethyl groups, respectively, were also tested. Figures 5 and 6 show larger spectral changes for both CuPC-C and CuPC-D, compared to the changes for CuPC-B. These results indicate that the higher stability of CuPC-B to ozone is unlikely to be due to simple steric hindrance.

The changes in cyan (C), magenta (M), and yellow (Y) 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.

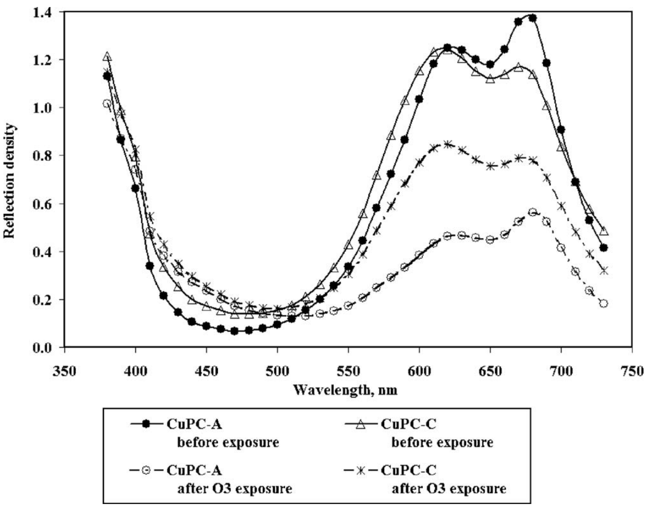


Figure 5. Ozone induced spectral changes in thermally transferred images of CuPC-A and CuPC-C.

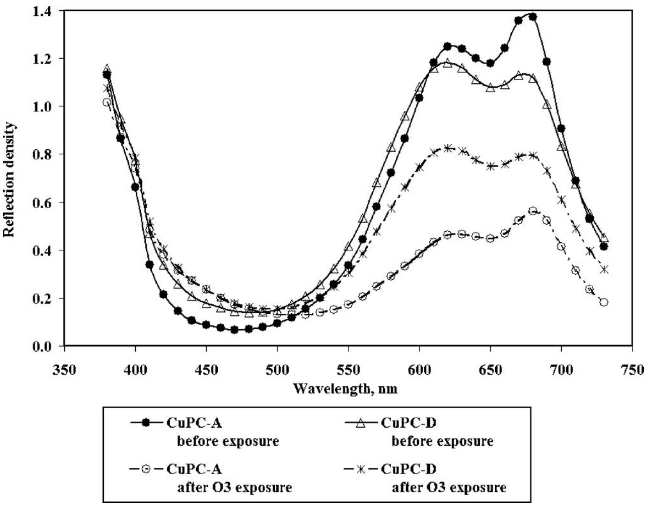


Figure 6. Ozone induced spectral changes in thermally transferred images of CuPC-A and CuPC-D.

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

Dyes	Density	*D*[C]	*D*[M]	*D*[Y]
CuPC-A	Initial	1.22	0.23	0.10
	After exposure	0.46	0.15	0.26
	Ratio, final/initial (%)	38	65	260
CuPC-B	Initial	1.20	0.31	0.25
	After exposure	1.19	0.31	0.26
	Ratio, final/initial (%)	99	100	104
CuPC-C	Initial	1.20	0.30	0.20
	After exposure	0.82	0.24	0.28
	Ratio, final/initia(%)	68	80	140
CuPC-D	Initial	1.15	0.30	0.20
	After exposure	0.80	0.23	0.26
	Ratio, final/initial (%)	70	77	130

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

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

A comparison of gradual cyan density loss with time of printed images of CuPC dyes due to exposure to ozone over an extended period of time is shown in Figure 7. The CuPC-A image shows 15% retention after 8.5 h of exposure, whereas the most stable CuPC-B image retains 73% of the initial cyan density under identical conditions. The other two dyes, CuPC-C and CuPC-D show much less density retention than CuPC-B, but are slightly more stable than CuPC-A. These results show the same trend in ozone stability of the CuPC dyes as observed after 1 h of ozone exposure.

The data indicate that the ozone stability of CuPC-B, containing allyl substituents, are considerably greater than that of the butyl or diethoxyethyl substituted CuPC-C and CuPC-D dyes. As discussed before, a comparison of the spectra of the four dyes shows that greater extent of H-aggregation as indicated by the blue shift in the spectrum of CuPC-B, may be associated with the observed ozone stability. The spectra of the control CuPC-A dye and the synthesized dyes, dissolved in methylene chloride, do not show any such difference. It is possible that the planar allyl groups facilitate the required rearrangement of the molecules to cause such aggregation more than the other substituents and result in a more stable form of dye in solid state, as in a transferred image. In addition, the allyl groups may also react with ozone and act as ozone scavengers, thus protecting the chromophore.

CONCLUSIONS

Difference in molecular substituents of copper phthalocyanine dyes produces large effects on ozone fading of the printed images. Images formed with the allyl substituted dye show greater ozone stability than those with butyl or diethoxyethyl substituted dyes. The allyl substituted dye also

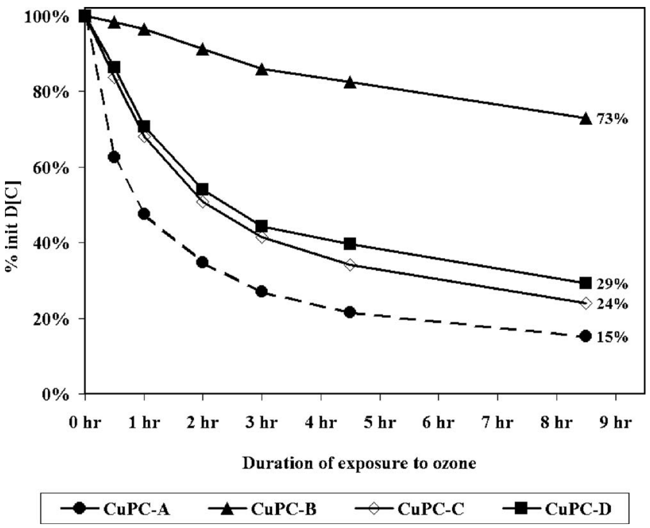


Figure 7. Rates of cyan density loss due to ozone exposure of thermally transferred images of CuPC dyes with varying substituents.

exhibits a larger extent of H-aggregation and blueshift in transferred images than the dyes containing other molecular substituents, when compared to their absorption spectra in solution. An increase in stability to exposure to ozone is likely to be due to the reaction of the allyl substituents with ozone, which accordingly act as ozone scavengers. Another possible factor may be the ease of formation of H-aggregates that are more stable than the monomeric dyes.

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