JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 49, Number 6, November/December 2005

Reduction of Ozone Fading of Copper Phthalocyanine Dyes by Non-traditional Antiozonants

Fariza B. Hasan▲
Polaroid Corporation, Waltham, Massachusetts, USA

Ozone fading of printed images has been an important concern in digital imaging industries. Copper phthalocyanine dyes, widely used in imaging products, have excellent light fastness, but they are highly susceptible to ozone fading. Although the detrimental effects of ozone on other industrial products, such as rubber are deterred by the addition of chemicals performing as antiozonants, mixing of dyes with these conventional antiozonants is usually not suitable for systems where the components are required to be in solution, due to the relatively lower solubility of these antiozonants in aqueous or solvent systems. Some of these efficient antiozonants also undergo oxidation, resulting in highly colored compounds, which also make them unsuitable for imaging products. The presence of suitable functional groups in the antiozonant molecules may reduce or eliminate both these problems. The results presented in this article show that several compounds, which are not used as typical antiozonants, improve ozone stability of copper phthalocyanine dyes to significant extents, with minimal colorimetric shifts. The effects of substituents on these antiozonant molecules are discussed in this article.

Journal of Imaging Science and Technology 49: 667–671 (2005)

Introduction

Copper phthalocyanine (CuPC) dyes are extensively used in imaging systems because of 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 studies related to exposure of images to ozone and its effects on image stability have been published in recent years, some of which are referred to in this article.[1–11]

Although phenylenediamines are effective antiozonants for several commercial products, such as rubber, where the oxidation due to exposure to ambient ozone can cause destruction of certain essential properties, they are not suitable as antiozonants for imaging products, because of the formation of highly colored products formed due to their reaction with ozone. Ozonations of anilines and *p*-phenylenediamines have been shown to proceed through an electron transfer reaction mechanism, which explains why the derivatives of *p*-phenylenediamine can be used as efficient antiozonants to prevent the degradation of rubber products caused by ozone.[12] The reaction products are also prone to polymerization which leads to highly colored products. For example, polyanilines (conducting polymers) are known to be readily produced by oxidation of anilines through aniline radical cation intermediates. The initial ozone attack has been hypothesized to occur at the nitrogen atom since it has lone pair electrons, which is consistent with numerous experimental observations.[12] Other methods used for minimizing degradation of rubber due to ozone, such as coating with impermeable materials is not easily applicable to imaging products. Organic phosphites, which act mainly as antioxidants have low solubility in water or common organic solvents, are also unsuitable for imaging systems. Aminoanthraquinone (AAQ) dyes contain the same functional groups, which are responsible for antiozonant property of *p*-phenylenediamines, but also contain electron withdrawing carbonyl groups in the fused ring systems. When coatings of these dyes are exposed to ozone, and compared with a coating of CuPC dye exposed under identical conditions, as shown in Fig. 1, the spectra of the AAQ dyes show almost no change, whereas the CuPC dye shows significant spectral change. It is expected that when these dyes are mixed with a CuPC dye, the ozone stability of the mixed dye system would be better than the CuPC dye. Also due to the relatively lower spectral absorptivity of the AAQ dyes compared to CuPC dye (Fig. 1) the absorption spectra of the mixtures are not expected to be significantly different from the CuPC dye. Since the AAQ dyes contain groups of varying electronegativities, several AAQ dyes, with substituents of varying electronic properties have been tested with a CuPC dye to determine the correlation between structure and antiozonant property.

Original manuscript received February 7, 2005

▲ IS&T Member

Corresponding Author: F. B. Hasan, currently at Zink Imaging, LLC, Waltham, Massachusetts, USA

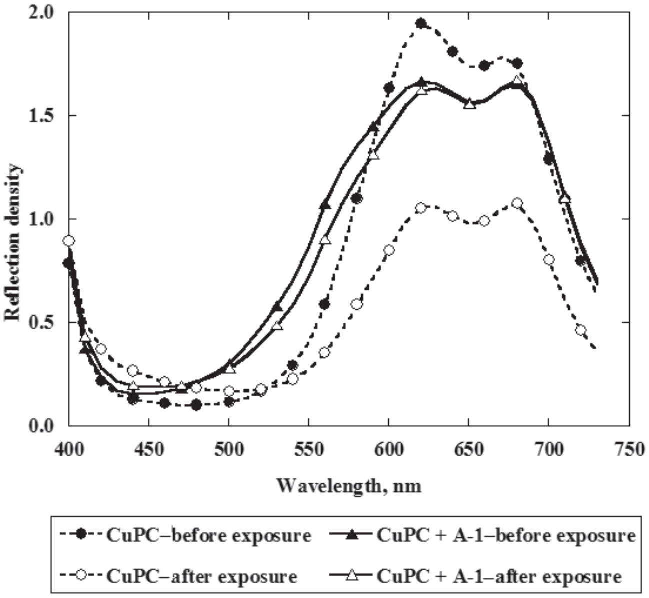


Figure 1. Reflection spectra of coatings of CuPC and AAQ dyes before and after exposure to ozone

Experimental Procedures

Test Methods

In order to simulate a printed digital image without any protective coating, CuPC dye and mixtures of CuPC and AAQ dyes were tested as coatings. Solutions of mixtures CuPC dye and AAQ dyes in organic solvents (*n*-butanol, methyl ethyl ketone, or other suitable solvent) were coated on PET sheets. The coatings to be tested for ozone resistance were exposed in an ozone chamber constructed from a Pyrex jar (1.2 ft^3) and a mercury-argon lamp. 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°C and relative humidity was 47–50%. The coatings were exposed to ozone for definite periods of time. For each set of experiments, a control coating, which contained a CuPC dye only at constant coating thickness for all the tests, 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 of the effective ozone concentration in the chamber for each set of experiments. 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 determine the antiozonant effects of the AAQ dyes on CuPC, it was not necessary to measure the exact concentration of ozone in the chamber. The extents of ozone stabilization due to the presence AAQ dyes were quantified by the extent of changes of the initial reflection densities (cyan, magenta and yellow) and colorimetric parameters (L^*, a^* and b^*) of the coated sheets before and after ozone exposure. A Gretag SPM50 densitometer was used for these measurements. The conditions for the measurements were: illumination = D50, observer angle = 2°, density standard = ANSI A, reflection standard = white base, and no filter. The molar ratios of AAQ dyes to CuPC dye were maintained between 1 and 2. Coatings of the AAQ dyes, without mixing with CuPC dye were also tested for ozone stability.

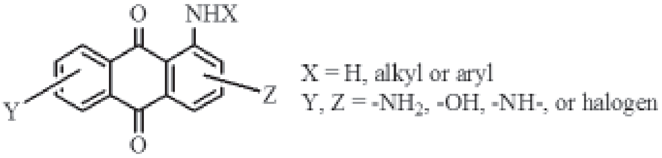


Figure 2. General structure of the aminoanthraquinones dyes

Aminoanthraquinones Tested

The selection of the commercially available AAQ dyes for testing with the CuPC dye was based on their spectral characteristics, with the intention to maintain the colorimetric change to a minimum. The aminoanthraquinone dyes used are represented by the general structure in Fig. 2.

Based on the substituents on the amino groups, the AAQ dyes tested are divided into three categories:

Type A: unsubstituted primary amino groups, –NH2
Type B: alkyl or hydroxyalkyl substituted secondary amino groups, –NHR (R = alkyl or hydroxyalkyl)
Type C: aryl substituted secondary amino groups, –NHAr (Ar = alkyl substituted phenyl)

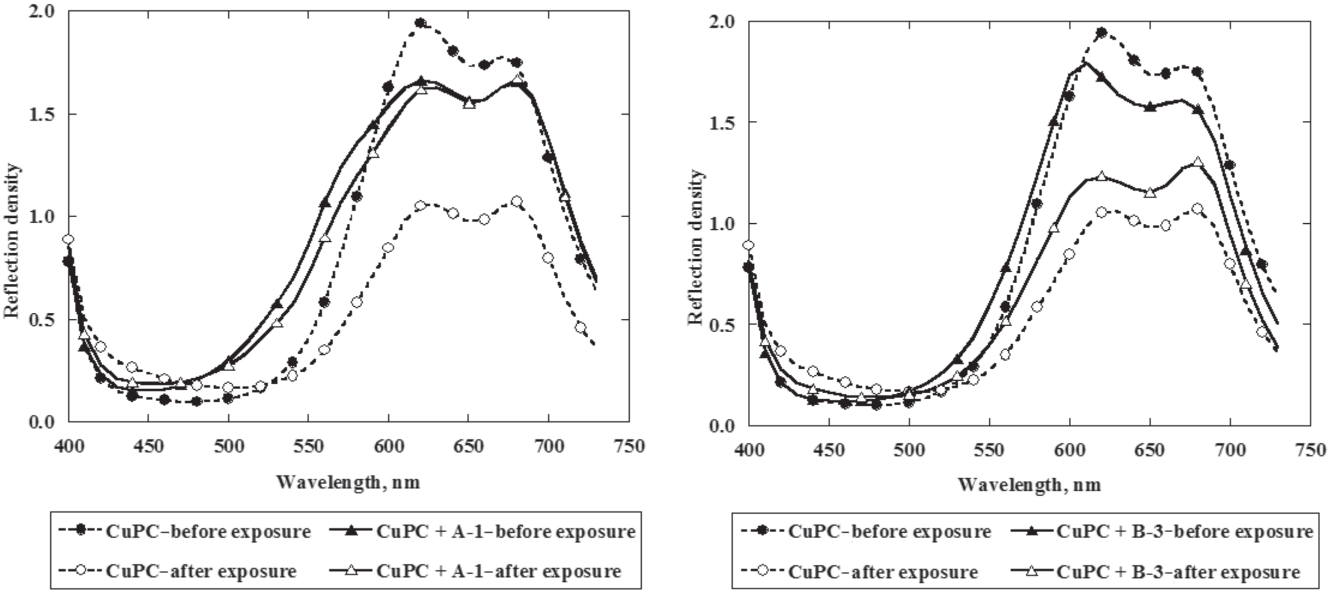
Other substituents on the rings are also present in many of these of dyes. The commercial names and the classification of the dyes according to their electronic structures are shown in Table I. In each of the categories the dyes are arranged in order of decreasing electron density on the amino groups, due to the presence of substituents on the nitrogen of the amino groups or other sites on the molecules. For the Type A dyes, which contain unsubstituted primary amino groups the difference in electron densities vary to a larger extent. Dyes of Types B and C contain secondary amino groups. The substituents on the amino group of Type B dyes are aliphatic and Type C dyes contain aromatic substituents. In general, the aliphatic substituents have less electron withdrawing effects and consequently higher electron densities on the amino group than aromatic substituents. Also the overall electronic effects on the amino groups of these dyes vary due to the differences in the substituents on the amino groups as well as other ring substituents. The dyes listed in each of these two categories show less variation than the dyes listed in Type A category.

Results and Discussion

As stated earlier in this article, Fig. 1 shows the reflection spectra of coatings of CuPC and three AAQ dyes, before and after exposure to ozone. Significant spectral change is apparent for the CuPC dye, whereas the changes for the AAQ dyes are nearly negligible. Figures 3(a) and 3(b) show the effects of ozone exposure on spectra of coatings of a cyan CuPC dye and mixtures of CuPC with two AAQ dyes, A-1 and B-3, respectively, which have different electron densities on the amino groups. Although the addition of AAQ dyes to CuPC dye causes some changes in the spectrum of CuPC dye, the CuPC dye shows significant reduction in density and spectral shift due to ozone exposure, but the changes are much less for the dye mixtures. The dye system containing A-1 shows very small change, whereas the system contain-

TABLE I. Classification of the AAQ Dyes Tested for Increasing Ozone Stability of CuPC

AAQ dyes	Amino groups and other substituents
Type A : Primary amines. Decreasing electron density on $-NH_2$ from A-1 to A-4	
Disperse Violet 1 (A1)	Diamine, $-NH_2$
1-Aminoanthraquinone (A-2)	Monoamine, $-NH_2$
Disperse Blue 56 (A-3)	Monoamine, $-NH_2$, with electron deficient ring substituents, –OH and –Br
Disperse Blue 60 (A-4)	Diamine, $-NH_2$, with fused ring containing electron deficient >C=O groups
Type B : Secondary amines. Decreasing electron density on –NHR, from B-1 to B-5	
Disperse Blue 14 (B-1)	Alkyl or hydroxyalkyl substituted secondary amines –NHR Varying R groups and other substituents in the molecule
Solvent Blue 59 (B-2)	
Solvent Blue 14 (B-3)	
Disperse Blue 7 (B-4)	
Disperse Blue 3 (B-5)	
Type C : Secondary amines. Decreasing electron density on –NHAr, from C-1 to C-3	
Solvent Blue 104 (C-1)	Aryl substituted secondary amines–NHAr Varying Ar groups other substituents in the molecule
Solvent Green 28 (C-2)	
Solvent Green 3 (C-3)	



(a) (b)

Figure 3. (a) Reflection spectra of coatings of CuPC with AAQ A-1 before and after exposure to ozone, (b) Reflection spectra of coatings of CuPC with AAQ B-3 before and after exposure to ozone

ing B-3, which has lower electron density than A-1, appears to show greater change due to exposure to ozone. The data listed in Table II show the ozone stabilizing effects of the AAQ dyes, as evident from the extent of retention of cyan density. However, the changes in cyan density only does not indicate the changes in other regions of spectra, which can cause significant hue shift and deterioration of image quality. In order to elucidate the extent of spectral changes, effects of ozone exposure on other colorimetric parameters, i.e., magenta and yellow densities, and the values of L^*, a^* and b^* after exposure to ozone are also included in Table II.

The result shows that after exposure to ozone the cyan density of CuPC without any added AAQ is 55% of the initial density. In addition to decrease in cyan density, significant colorimetric shift also occurs, as indicated by decrease in magenta density and increase in yellow density. The presence of AAQ dyes has varying effects on these parameters. Since the changes occurring due to ozone exposure are not uniform over the entire spectral range the extents of change of all the parameters are not equal. However, the dyes, which appear to be most efficient in retaining cyan density, also cause less overall spectral change, as evident from

TABLE II. Effects of AAQ Dyes on Ozone Exposure of Coatings of Equimolar Ratios of CuPC and AAQ Dyes, Exposure Time = 1 hour

Type of AAQ added	Density retained			Change after ozone exposure		
	D[C]	D[M]	D[Y]	Delta *L**	Delta *a**	Delta *b**
None (CuPC only)	55%	85%	192%	6.68	6.61	25.71
A-1	98%	86%	125%	3.87	–11.52	9.93
A-2	94%	81%	84%	5.00	–6.75	–1.42
A-3	82%	82%	124%	5.40	–6.94	12.98
A-4	55%	84%	183%	7.28	11.00	24.10
B-1	86%	85%	131%	3.92	–4.77	11.26
B-2	84%	86%	138%	3.77	–6.34	10.84
B-3	76%	77%	117%	7.47	–4.87	17.18
B-4	64%	83%	150%	6.34	5.82	18.62
B-5	62%	76%	182%	8.31	5.21	23.01
C-1	70%	88%	153%	5.15	4.81	17.14
C-2	61%	85%	121%	6.35	11.27	16.07
C-3	57%	81%	164%	7.26	11.09	22.11

TABLE III. Effects of Molar Ratio Variation of AAQ to CuPC on Ozone Stability of CuPC, Exposure Time = 1 hour

AAQ	Molar ratio, AAQ : CuPC	Cyan density retained
A-3	1.0	82%
	1.5	91%
A-4	1.0	55%
	1.5	57%
B-4	1.0	64%
	1.5	69%
C-3	1.0	57%
	1.5	58%

a comparison of all the spectral and colorimetric parameters.

The data in Table II indicate that the efficiency of the added dyes as antiozonants, as evident from the higher fraction of cyan density retained and lower colorimetric changes, depends on the electronic structure of the molecule. In each of the categories a decrease in the electron density on the amino group, due to the presence of substituents on nitrogen or other parts of the rings, results in a decrease of the antiozonant property of the dye.

The effects of increasing levels of some of the AAQ dyes, which have moderate to low efficiency, on ozone stability of CuPC dye are shown in Table III. Greater ozone stability is observed at higher molar ratios of the more efficient dyes, e.g., A-3 and B-4. However, the increase is insignificant with less efficient dyes, i.e., C-3 and A-4, which may require much larger levels to be effective.

In order to compare the stabilization effects of AAQ dyes on CuPC exposed for a definite length of time with continuous exposure to ozone the rates of density loss due to exposure to ozone of CuPC dye and mixtures of CuPC dye with four AAQ dyes were compared. Two Type A dyes, A-1, a diamine and A-2, a monoamine were tested, because of their significantly different electronic structures. One of each of the types B and C dyes were tested, for the reason that although both contain secondary amino groups, the electronic structures of the substituents and their effects as antiozonant are different, B-3 being moderately efficient and C-3 appears to have considerably smaller effect than the other dyes of these two categories (Table II).

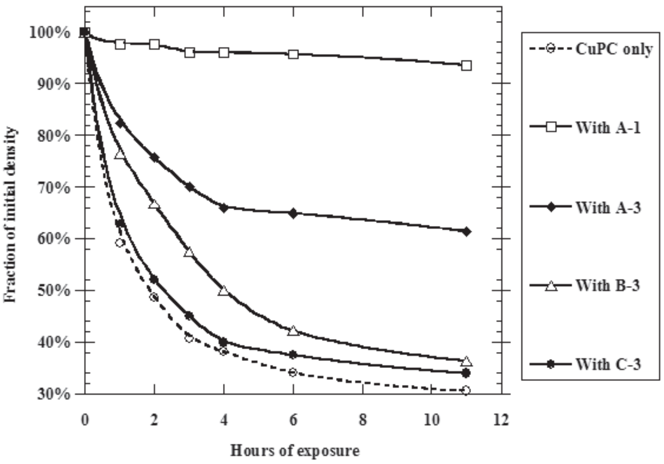


Figure 4. Effects of ozone exposure on the rates of change of reflection density of coatings of CuPC dye and mixtures of CuPC and AAQ dyes.

Figure 4 shows the fraction of initial cyan density retained for each of the systems after definite intervals of time. Pseudo-first order rate plots for the loss of density under these conditions are shown in Fig. 5 and the calculated apparent rate constants are listed in Table IV. It is evident from these data that the substituents on the AAQ dyes have significant effects on the rate of density loss, which is a measure of the antiozonant property. The rate of density loss in presence of A-1 is more than an order of magnitude lower than of CuPC dye, or when mixed with the less efficient AAQ dyes. Clearly the presence of two unsubstituted amino groups in the AAQ dye molecule, A-1 causes it to be more efficient than the dye with one unsubstituted amino group, A-2, or substituted amino groups, B-3 and C-3. The dye B-3, containing alkyl substituted amino groups is more effective than C-3, which contains aryl substituted amino groups. The kinetic results are in agreement with the data obtained after a fixed exposure time, as listed in Table II.

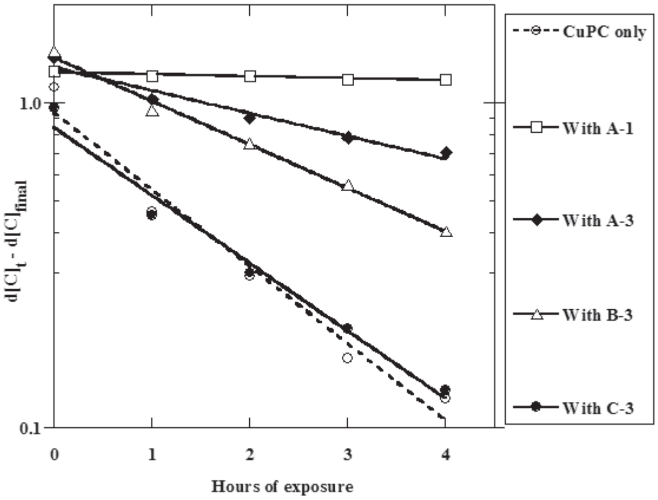


Figure 5. Pseudo-first order rate plots for density loss due to ozone exposure of CuPC dye and mixtures of CuPC and AAQ dyes.

As described before, it is apparent from the reflection spectra of coatings of mixtures of CuPC and the AAQ dyes (Figs. 3(a) and 3(b)) cause slight changes of the original spectrum of CuPC. However, since the colorimetric changes of the mixtures are significantly less than CuPC when exposed to ozone, the addition of dyes such as A-1 or A-2 would increase stability of images exposed to ambient ozone levels to a large extent, and will outweigh the slight spectral shifts. Moreover, since these results are from accelerated ozone exposure test, which is a standard practice in imaging industries, lower levels of the more efficient dyes may be adequate to reduce ozone fading in long-term tests, and consequently reduce the change of the color of CuPC dyes.

Although the exact mechanism of the antiozonant function of the AAQ dyes under the conditions of these experiments has not been established, the data indicate that the presence of electron donating groups in AAQ dye molecules increases their effectiveness as antiozonant for CuPC dye. Several studies related to reactions of anilines and phenylenediamines with ozone and other oxidants in solution and gas phase have been published,[12,13] which indicate the effects of substituents on the ease of oxidation. If the AAQ dyes in solid phase, such as in coatings or printed images, also follow similar mechanism the antiozonant property may be due to scavenging of ozone, which essentially reduces the concentration of ozone available to react with CuPC.

Table IV. Effects of AAQ Dyes on Ozone Stability of CuPC Dye

Decreasing electron density on –N<, from A-1 to C-3
Pseudo-first order rate constants

AAQ Dye Added	Pseudo-first order rate constant for loss of cyan density, hr^{-1}
None (CuPC dye only)	0.545
A-1 (di –NH$_2$)	0.014
A-2 (mono –NH$_2$)	0.162
B-3 (–NHR)	0.308
C-3 (–NHAr)	0.480

Conclusions

- Aminoanthraquinones dyes can be used as antiozonants for copper phthalocyanine dyes.
- Coatings of mixtures of copper phthalocyanine dyes with aminoanthraquinones dyes show less fading and spectral shift when exposed to ozone.
- The efficiency of the added aminoanthraquinone dye as antiozonant depends on the electronic structures of the aminoanthraquinones dyes and shows significant dependence on the substituents. Higher electron density due to the substituents increases antiozonant property of the dye.

Acknowledgment. The author wishes to express sincere appreciation to Michael A. Young for providing the chamber for ozone exposure and Polaroid Corporation for supporting the research project.

References

1. M. Berger and H. Wilhelm, *Proc. IS&T's NIP19*, (IS&T, Springfield, VA, 2003), pp. 438–443.
2. M. Thornberry and S. Looman,, *Proc. IS&T's NIP19*, (IS&T, Springfield, VA, 2003), pp. 426–430.
3. K. Kitamura, Y. Oki, H. Kanada and H. Hayashi, *Proc. IS&T's NIP19*, (IS&T, Springfield, VA, 2003), pp. 415–419.
4. D. Bugner, R. Van Hanehem, P. Artz,and D. Zaccour, *Proc. IS&T's NIP19*, (IS&T, Springfield, VA, 2003), pp. 397–401.
5. J. Geisenberger, K. Saitmacher, H. Macholdt and H. Menzel, *Proc. IS&T's NIP19*, (IS&T, Springfield, VA, 2003), pp. 394–395.
6. S. Wakabayashi, S., T. Tsutsumi, M. Sakakibara, Y. Nakano and Y. Hidaka, *Proc. IS&T's NIP19*, (IS&T, Springfield, VA, 2003), pp. 203–206.
7. R. A. Barcock and A. J. Lavery, *J. Imaging Sci. Technol.*, **48**(2), 153–159 (2004).
8. D. Brignone, D, W. Fontani and A. Sismondi, A, *Proc. IS&T's International Symposium on Photofinishing Technology*, (IS&T, Springfield, VA, 2004), pp. 47–50.
9. C. Halik and S. Biry, Stephane. *Asia Pacific Coatings Journal*, **16**(4), 20–21 (2003).
10. S. Kiatkamjornwong, K. Rattanakasamsuk and H. Noguchi, *J. Imaging Sci. Technol.*, **47**(2), 149–154 (2003).
11. A. Kase, H. Temmei, T. Noshita, M. Slagt and Y. Toda, *Proc. IS&T's NIP20*, (IS&T, Springfield, VA, 2004), pp. 670–672.
12. X. Zhang and Q. Zhu, *J. Org. Chem.*, **62,** 5934–5938 (1997), and references cited therein.
13. N. S. Lawrence, E. L. Beckett, J. Davis, and R. G. Compton, *Analyst*, **126,** 1897–1900 (2001).