

Synthesizing Premetallized Acid Dyes Based on Environmental Considerations

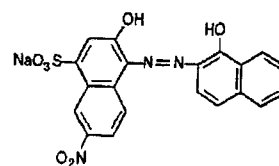
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Metallized azo dyes derived from ortho, ortho'-bis (hydroxy) monoazo compounds constitute an important class of colorants for the dyeing of wool and nylon for applications requiring high stability to prolonged and repeated exposure to UV radiation and to washing,^{1,2} especially in alkaline media. In the case of fast and bright shades for wool, chromium is presently by far the best metal to use, as other metals have produced complexes having inferior fastness to light and washing.^{1,3-5} The first chromium (Cr) complexes developed were actually generated directly on wool fibers by applying appropriately substituted unmetallized chrome dyes to wool fol-

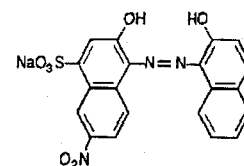
lowed by treating the resultant dyed substrate with Cr(VI) or Cr(III) compounds.^{2,6} This method led to the development of dyes such as C.I. Mordant Black 11, a high volume dye for the production of black shades on wool where fast dyeings at an economical price are needed.⁷ Although this method improved the light- and wet-fastness of the dull alkali-sensitive dyeings obtained using the corresponding metal-free dyes, the chrome dyeing process also afforded wastewater effluents from dyehouses containing levels of metal ions deemed harmful to the environment.⁴ This was especially true when Cr(VI) was used, as hexavalent chromium is toxic to many forms of aquatic life as well as to the organisms employed to degrade sewage in biological degradation facilities.^{4,7,8} The observed toxicity led environmental authorities to discourage the continued use of chrome dyes and to impose severe limitations on the concentration of both Cr(VI) and Cr(III) in effluents. Efforts to comply with these restrictions led in turn to the development of wastewater treatment methods for lowering Cr levels prior to discharging an exhausted dye bath. Typical methods developed include precipitation of the metal followed by collection by filtration, and reduction of residual Cr(VI) to Cr(III) followed by complexing the resultant Cr(III) ions *in situ* and absorbing them onto the dyed wool fiber with the aid of a chemical auxiliary.⁴

During the time when methods for solving environmental concerns arising from chrome dyeing were being pursued, it was widely believed that the corresponding iron (Fe) complexes were so inferior to Cr complexes in both fastness and brightness that they could not be seriously considered as viable alternatives. Perhaps this is because the early complexes made were actually 1:1 rather than the presently more desirable 1:2 complexes.⁹ This in turn probably led scientists away from Fe complexes as a method for produc-

ing environmentally friendly dyeings on wool and nylon, and towards the development of a method for dyeing textiles with metallized dyes in which the metal was inserted into the dye ligand prior to dyeing the substrate, as another way to address concerns raised about the pollution problem caused by chrome dyeings. Thus, Mordant Black 11 (MB 11) and its commercially important isomer Mordant Black 1 (MB 1) evolved into premetallized dyes such as Acid Black 52 (AB 52), Acid Black 107 (AB 107) and Acid Black 172 (AB 172). Fig. 1 shows the chemical structures of these dyes. As that work unfolded, it was determined that the 1:2 premetallized dyes were preferred over the corresponding 1:1 complexes. Interestingly, it was also determined that the toxicity level of residual Cr in exhausted premetallized dye baths was often greater than that observed in exhausted afterchrome dye baths when a method for reducing residual Cr in the latter type of dye bath was employed.⁴



Mordant Black 11



- Mordant Black 1 (unmetallized dye)
Acid Black 52 (1:1/1:2 Cr complex)
Acid Black 107 (1:2 Cr mixed complex with 4 other monoazo dyes)
Acid Black 172 (1:2 Cr complex)

Fig. 1. Chemical structures of Mordant Black 11 (top) and Mordant Black 1, Acid Black 52, Acid Black 107 and Acid Black 172 (bottom).

ABSTRACT

As part of a continuing research program aimed at plausible approaches to synthetic dyes based on toxicological considerations, a group of premetallized iron complexed monoazo dyes were synthesized as potential alternatives to presently used high volume Cr- and Co- containing monoazo acid dyes for nylon and wool. This approach takes advantage of the environmentally friendly property of Fe, and draws from the established utility of Fe complexes as brown dyes for certain protein substrates. This investigation has led us to two black Fe complexes having fastness properties comparable to the Cr analogs on both wool and nylon. In addition, we report results from *in vitro* testing of the Fe complexes for genotoxicity.

KEY TERMS

Dye Synthesis
Environment
Fe Complex Dyes
Monoazo Dyes
Nylon
Wool

to remove toxic metal ions resultant from both the manufacture of Cr-based metallized dyes and the application of these dyes to wool, nylon and leather substrates. The present work constitutes another step in the evolution of lightfast and washfast black dyeings for wool and nylon. In essence, this research provides a mechanism for the environmentally friendly delivery of black shades to natural and synthetic polyamides without the use of Cr(VI) or Cr(III) and without compromising the desirable fastness properties of the Cr complexes, by using 1:2 Fe-complexed dyes shown in Fig. 2. The specific structures serving as the focus of this paper are dyes 1 and 2 shown in Fig. 3.

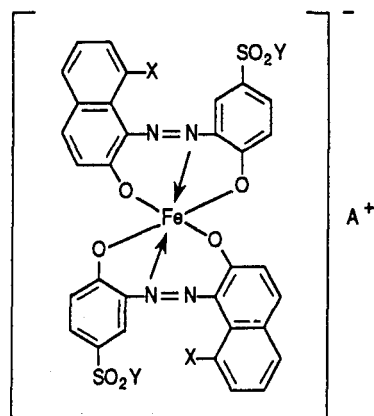


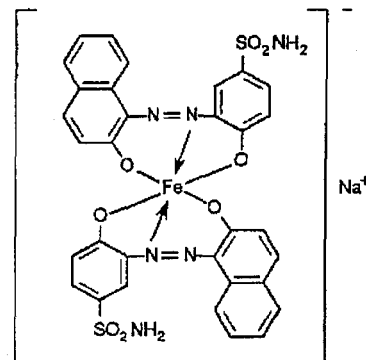
Fig. 2. Chemical structure for 1:2 Fe-complexed dyes, where X is H or NHAc, Y is amino and A is Na.

Until now, it has been presumed that the use of Cr-based dyes is essential to the generation of fast black dyeings on wool and nylon. Consequently, it is thought that the removal of Cr-based dyes from commerce would be unduly injurious to operations dependent upon the superior fastness properties heretofore unachievable through the use of an environmentally friendly metal such as iron.

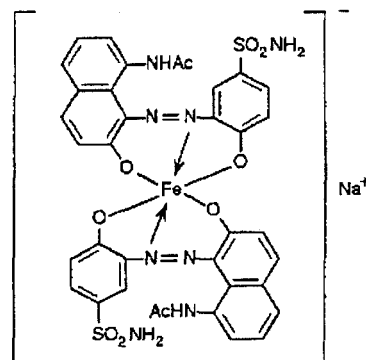
This research represents a departure from conventional approaches to protecting the environment through the use of wastewater treatment methods

Experimental

The method used in synthesizing dyes 1 and 2 involved the diazotization of 1-hydroxy-2-aminobenzenesulfonamide followed by coupling with either 2-naphthol or 1-acetylamino-7-naphthol, and converting the metal-free monoazo dye to a 1:2 Fe complex using either Fe(II) sulfate or Fe(III) sulfate at slightly alkaline pH, or using Fe(III) sulfate in the presence of sodium formate at slightly acidic pH.^{10,11} Formation of the target 1:2 Fe complexes was confirmed by using negative ion FAB mass spectrometry with 3-nitrobenzyl alcohol as the matrix. In each case, the molecular ion [M]⁻ and/



1



2

Fig. 3. Chemical structure for dyes 1 (top) and 2 (bottom).

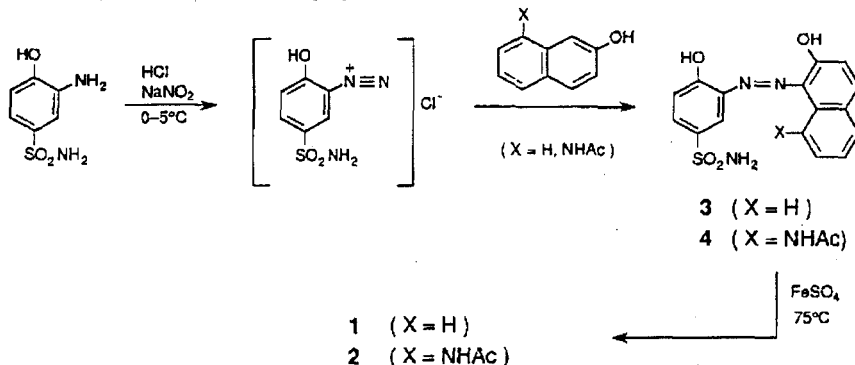


Fig. 4. Synthesis of dyes 1 and 2.

Table I. Lightfastness Data^a for Dyes 1 and 2 Compared to AB 172

Dye No.	Type of Metal	Depth of Dyeing	Lightfastness ^b			
			Wool		Nylon	
			225.6 kJ/m ²	451.2 kJ/m ²	225.6 kJ/m ²	451.2 kJ/m ²
AB 172	Cr	2%	2	1	1-2	<1
AB 172	Cr	6%	4	4	1-2	<1
1	Fe	2%	1-2	<1	<1	<1
1	Fe	6%	4	3	2-3	1
2	Fe	2%	1-2	<1	<1	1
2	Fe	6%	5	4	2	1

^a Derived from the standard test employing the Atlas Ci65 Weather-Ometer to evaluate potential automotive-grade dyes.
^b Scale ranges from a low of 1 to a high of 5.

Table II. Crockfastness Data^a for Dyes 1 and 2 Compared to AB 172

Dye No.	Type of Metal	Depth of Dyeing	Crockfastness ^b	
			Wool	Nylon
AB 172	Cr	2%	5	4-5
AB 172	Cr	6%	4-5	4-5
1	Fe	2%	4-5	4-5
1	Fe	6%	4-5	4-5
2	Fe	2%	4-5	4-5
2	Fe	6%	4-5	4-5

^a Derived from AATCC Test Method 8-1985.
^b Scale ranges from a low of 1 to a high of 5.

Table III. Washfastness Data^a (Change in Color) for Dyes 1 and 2 Compared to Some Commercial Acid Blacks

Dye No.	Type of Metal	Depth of Dyeing	Color Change ^b	
			Wool	Nylon
AB 63	Cr	2%	4-5	4-5
AB 63	Cr	6%	4-5	4-5
AB 107	Cr	2%	4-5	5
AB 107	Cr	6%	4-5	5
AB 172	Cr	2%	5	4-5
AB 172	Cr	6%	4-5	4-5
1	Fe	2%	5	5
1	Fe	6%	4-5	5
2	Fe	2%	4-5	5
2	Fe	6%	5	5

^a Derived from AATCC Test Method 61-1986, Test No. 2A.

^b Scale Ranges from a low of 1 to a high of 5.

Table IV. Washfastness Data^a (Staining of Fibers) for Dyes 1 and 2 Compared to Some Commercial Acid Blacks

Dye No.	Type of Metal	Depth of Dyeing	Fiber Staining ^b			
			Dyed Wool		Dyed Nylon	
			A	B	A	B
AB 63	Cr	2%	4-5	3-4	4-5	4
AB 63	Cr	6%	4	3-4	4-5	3-4
AB 107	Cr	2%	5	4-5	4-5	4-5
AB 107	Cr	6%	4-5	3	4-5	3-4
AB 172	Cr	2%	4-5	4	4-5	4
AB 172	Cr	6%	4-5	4-5	4-5	3-4
1	Fe	2%	4	4	4	3-4
1	Fe	6%	3-4	3-4	3-4	3
2	Fe	2%	4	3-4	3-4	3
2	Fe	6%	3-4	3	3-4	3

^a Derived from AATCC Test Method 61-1986, Test No. 2A;

^b Scale ranges from a low of 1 to a high of 5;

A = Staining of Wool, B = Staining of Nylon.

or the pseudomolecular ion [M-Na] was detected.

The synthesized dyes were applied to nylon and wool fabric at a 2-6% depth of shade and 90-100% exhaustion.¹⁰ and the dyed fabrics were evaluated for lightfastness, washfastness and crockfastness according to established procedures.¹²

Results and Discussion

Fig. 4 shows the reaction scheme used to prepare dyes 1 and 2. The two unmetallized dyes (3 and 4) were isolated by precipitation at neutral pH and required no further purification prior to forming the corresponding Fe complexes.

When dyes 1 and 2 were applied to textiles at a 4-6% depth of shade, black dyeings resulted having fastness properties comparable to those arising from the application of some commercial acid blacks. See Tables I-IV for comparisons. It is clear from the data in Table I that the 1:2 Fe complex (dye 1) has good lightfastness at the higher depth of shade, and that lightfastness is appreciably better on wool versus nylon, both results being in line with those observed using the corresponding Cr complex Acid Black 172 (AB 172). In addition, it is clear that the in-

roduction of an acetamido group (NHAc) into the 8-position of the naphthalene ring further enhances lightfastness on wool, without producing a similar improvement on nylon. It is worth pointing out that the lightfastness of dye 2 is quite good on wool even at 451.2 kJoules when the depth of shade is 4% (lightfastness = 3-4) or 6% (lightfastness = 4). Similarly, Table II shows that the crockfastness (dry) is not adversely affected by using the Fe complexes in lieu of Acid Black 172, irrespective of the shade depth.

Examination of the washfastness data shown in Tables III and IV allows one to conclude that color change would not be injured by substituting either dye 1 or 2 for the commercial dyes Acid Black 63 (shown in Fig. 5), 107, or 172; and it is believed that Acid Black 52 could also be a target for substitution. On studying the fiber staining results it is clear that the commercial dyes have an edge, although the data arising from the use of 1 and 2 are comfortably within the range of acceptability.

In addition to assessing the fastness properties of dyes 1 and 2, mutagenic properties were determined using the Ames test.¹³ The results are summa-

rized in Table V and in Figs. 6 and 7. The Ames test was carried out at dose levels of 0-1 mg/plate using 2-nitrofluorene as the positive control and deionized water as the negative control. Figs. 6 and 7 provide the relationship between the amount of dye used (dose level; X-axis) and the number of bacteria colonies counted at a given dose (Y-axis). The plotted data are tabulated in the upper right-hand corner of each figure, where dose is the amount of dye used in milligrams (mg) and the plate counts are the number of bacteria colonies resulting from that amount of sample. The first entry in the tabulation results from testing the positive control. In each case, duplicate plates were generated in each experiment. Note that data from both plates are plotted on the same graph; hence, double points appear at each position along the lines drawn. A compound is judged as mutagenic when the number of plate counts at a given dose exceeds twice the number of plate counts at dose = 0 (the so-called number of spontaneous revertant colonies). The higher the number of plate counts goes above this threshold value, the more mutagenic a compound is judged to be. This means a dye can be judged a weak, moderate or strong mutagen. Dyes 1 and 2 were negative in the absence or presence of rat liver S9 (enzyme) acti-

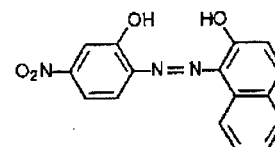
Table V. Mutagenicity Data for Dyes 1 and 2 Resulting from the Model of Stead¹⁴ and Bernstein¹⁵

Tester Strain	Activation	Stead		Bernstein	
		Dye 1	Dye 2	Dye 1	Dye 2
TA 98	-	NEG	NEG	NEG	NEG
TA 98	+	NEG	NEG	NEG	NEG
TA 158	-	NEG	NEG	NEG	NEG
TA 158	+	NEG	NEG	NEG	NEG

NEG = Nonmutagenic

- = without metabolic activation

+ = with metabolic activation



Acid Black 63 (1:2 Cr complex)

Fig. 5. Chemical structure for Acid Black 63 (1:2 Cr complex).

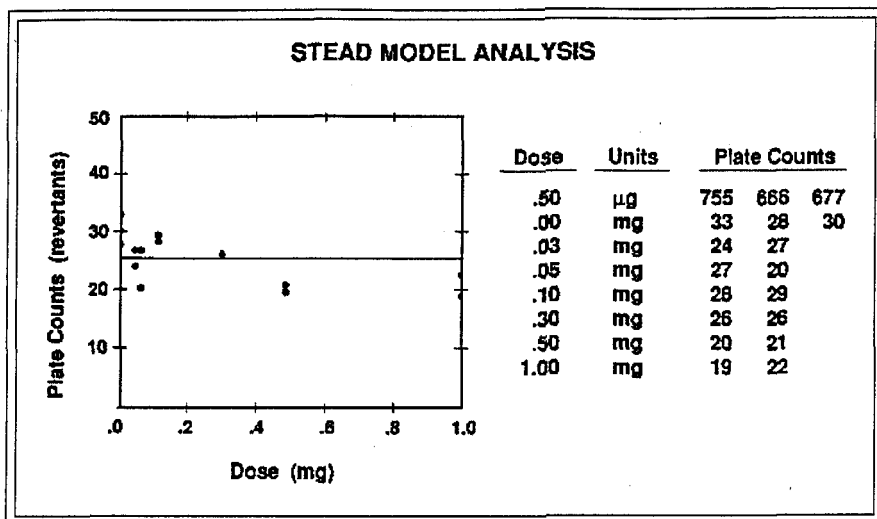


Fig. 6. Stead Model Analysis of the mutagenicity data from testing dye 2 in TA 98.

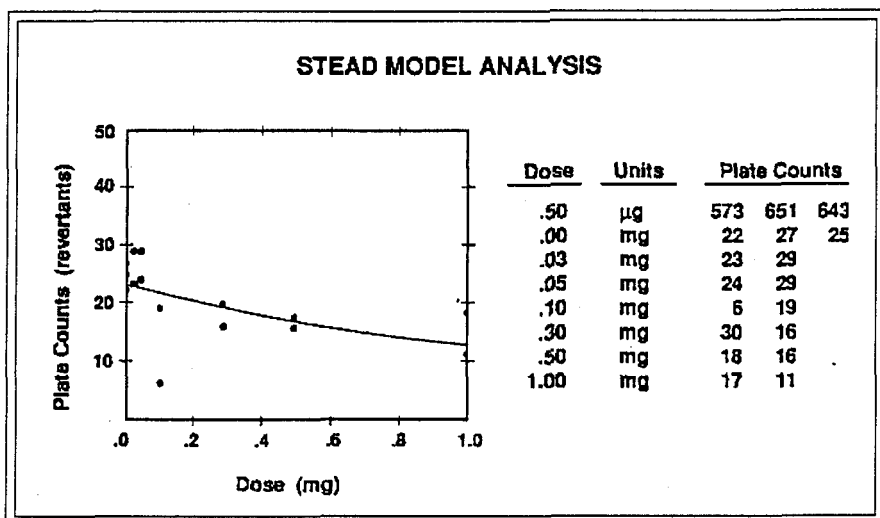


Fig. 7. Stead Model Analysis of the mutagenicity data from testing dye 2 in TA 1538.

vation. A negative response in the absence of S9 means that neither dye is a direct-acting mutagen, and a negative response in the presence of S9 means that neither was metabolized upon incubation with the enzyme system to produce a mutagenic substance.

Summary

This paper outlines an alternative approach to solving the environmental problem associated with the use of Cr-based metallized azo dyes to deliver black shades on polyamide and protein substrates. The approach affords methods for both the synthesis of metallized dyes and the generation of black dyeings using those dyes without employing metals designated as priority pollutants at any stage in either process. The key element of the approach is the use of black 1:2 Fe complexes of azo dyes in lieu of currently used Cr-based complexes without compromising the desirable high fastness properties of the latter complexes, an accomplishment heretofore assumed unachievable.

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