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SYNTHETIC DYES BASED ON TOXICOLOGICAL CONSIDERATIONS

PI: Harold Freeman
Industrialist: Abraham Reife
Research Associate: Jolanta Sokolowska-Gajda, David Hinks
Graduate Students: Laura Cleveland, Julie Peterson, Jason Lye

HIGHLIGHTS

* Results from Ames mutagenicity assays show that the Fe-complexed azo dyes on which we filed for, and are soon to receive, a patent are indeed nonmutagenic.

* A new group of Fe-complexed dyes have been synthesized and found to include structures having very good all-around fastness properties on nylon as well as wool.

* The synthesis of Fe-complexed dyes having violet and blue colors has been achieved.

Objectives

This project pertains to the design, synthesis, and evaluation of dyes for textiles that would be environmentally friendly alternatives to certain metallized and dyes and hydrophobic dyes that have been labeled as "a potential risk" to human health or the environment. The basic theme is molecular design that includes potential toxicological behavior as a key parameter in the design of new dyes for textile applications. The design phase includes: 1) The identification of alternatives to metals classified by EPA as priority pollutants (e.g. Cu, Cr); 2) Characterization of the metabolites generated from certain hydrophobic azo dyes, and the mechanism associated with their formation; 3) Determination of the role of metals in enhancing azo dye lightfastness; and 4) An assessment of the fate of iron complexed dyes in an aquatic environment.

Introduction

Our work during the past year has been devoted to the continued exploration of Fe-complexed dyes as potential alternatives to important commercial metallized dyes containing Cr, Cu, or Co as the metal. Key goals for the year included the design, synthesis and analysis of Fe-complexed dyes 1) which expand the range of colors developed so far to include red and blue shades and 2) which possess good lightfastness on nylon as well as wool. During our systematic search for plausible structures, we uncovered some interesting candidates in the formazan family. Several representatives were synthesized and evaluated in a battery of fastness and mutagenicity tests.

This report provides a summary of work pertaining to 1) assessment of the genotoxicity of selected Fe-complexed formazan dyes prepared during the past year; and 2) comparison of the fastness properties of our new Fe complexed dyes to important commercial metallized dyes (Cr or Co complexes) of the same color.

Results and Discussion

Metallized Dyes - FASTNESS PROPERTIES

In addition to producing fast black shades, the target formazans afforded violet and blue shades. We are not aware of previous reports in the literature in which such colors are reported for Fe-complexed dyes. Consequently, a patent application has been prepared to cover this entire family of new colorants.

The blue and violet iron complexes were evaluated in standard AATCC tests for washfastness, crockfastness, and lightfastness, along with the new black and brown Fe complexes were. A summary of the finalized results for five of the key dyes is given in Tables 1-3. All dyes (**I-VI**) are Fe complexes of the formazan system, which heretofore has found greater utility as a substrate for fiber reactive dyes. We found that these new dyes have comparable lightfastness on nylon and wool (cf. Table 2). Previously made Fe complexes suffered the disadvantage of low lightfastness on nylon. In addition, Tables 2-3 show that the other key fastness properties quite good on both fiber types.

As a consequence of the promising results of Table 1, the formazan complexes were evaluated as potential automotive dyes for nylon carpet. Dyes **II** and **IV** were found to have good to very good fastness at 225.6 kJ/m^2. Both have fastness on wool that is comparable to that of the widely used dye Acid Black 172 (a 1:2 Cr complex), and superior lightfastness on nylon compared to the commercial dye. We are now searching for an industrial partner to assist in assessing the commercial utility of the new formazan dyes, and intend to seek a patent on these colorants.

Table 1. Lightfastness of some new Fe-complexed formazan acid dyes.

Dye	**Shade Depth**	**Color**	**Lightfastness**			
			Wool		**Nylon**	
			40h	80h	40h	80h
I	2%	Blue	3-4	3	4-5	5
II	2%	Dk. Brn.	5	4-5	4-5	3-4
	6%	Black	4-5	4-5	4-5	4-5
III	2%	Red-Blue	4-5	4-5	4-5	4
IV	2%	Dk. Brn.	4-5	4-5	4-5	4
	6%	Black	5	5	4-5	4-5
V	2%	Brown	4	3-4	4-5	4
VI	2%	Red-Brn	5	4	4	3

Lightfastness was evaluated using an Atlas ES25 weatherometer according to AATCC TM 16-1990 for textile materials.

Table 2. Washfastness of some new Fe-complexed formazan acid dyes.

Dye	Shade Depth	Washfastness					
		Color Change		Fiber Staining			
		Wool	Nylon	Dyed Wool		Dyed Nylon	
				A	B	A	B
I	2%	5	5	5	4-5	5	4-5
II	2%	5	5	5	4-5	4-5	3-4
	6%	5	5	4-5	4-5	4-5	4-5
III	2%	5	5	4-5	4-5	4-5	4
IV	2%	5	5	4-5	4-5	4-5	4
	6%	5	5	4-5	4	4-5	4
V	2%	5	5	4-5	4	4-5	4-5
VI	2%	5	5	5	4-5	4-5	4-5

A = staining of wool
B = staining of nylon

Table 3. Crockfastness of some new Fe-complexed formazan acid dyes.

Dye	Shade Depth	Crockfastness Wool	Nylon
I	2%	5	5
II	2%	5	5
	6%	4-5	4-5
III	2%	5	5
IV	2%	5	5
	6%	4-5	5
V	2%	5	5
VI	2%	5	5

Table 4. Lightfastness of Dyes **II**, **IV**, and Acid Black 172 in the GM Test for Automotive Textiles.

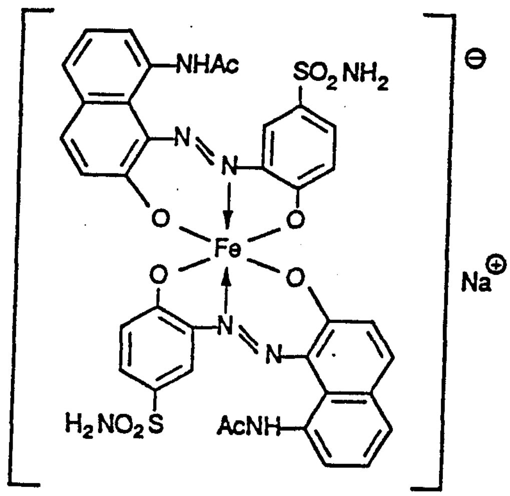
Dye	**Shade Depth**	**Lightfastness***			
		Wool		**Nylon**	
		225.6	451.2	225.6	451.2
II	2%	3	2	1-2	1
	6%	5	4-5	4-5	3
IV	2%	3-4	2	1	1
	6%	4-5	4	4-5	3-4
AB 172**	2%	2	1	1-2	1-2
	6%	4	4	<1	<1
AB 52	2%	3-4	2-3	4	2
	6%	4-5	3-4	4	2

* Values are kJ/m^2

** Acid Black 172

Metallized Dyes - GENOTOXICITY

Ames mutagenicity testing has been conducted on all the metallized azo dyes prepared so far. As an example, Figures 1 and 2 show results from the Ames analysis of dye **VII**. The data shown result from mutagenicity testing of **VII** in bacteria strain TA100 with and without S9 metabolic activation. It is clear from these graphs that the Fe complex lacks the mutagenicity exhibited by Acid Black 172 (the Cr analog). Comparable results were obtained from evaluating formazan dyes **I-VI** in the Ames test.



Dye VII

Conclusions

It is clear from the results of this study that Fe complex dyes constitute a family of dyes worth considering as potential alternatives to metallized dyes based on Cr, Co, and Cu. It has been demonstrated possible to utilize the former type compounds without compromising the desirable fastness properties of the latter types. Remaining to be demonstrated it the generation of a family of Fe complexes which span the entire color spectrum. We believe that this goal can be achieved.

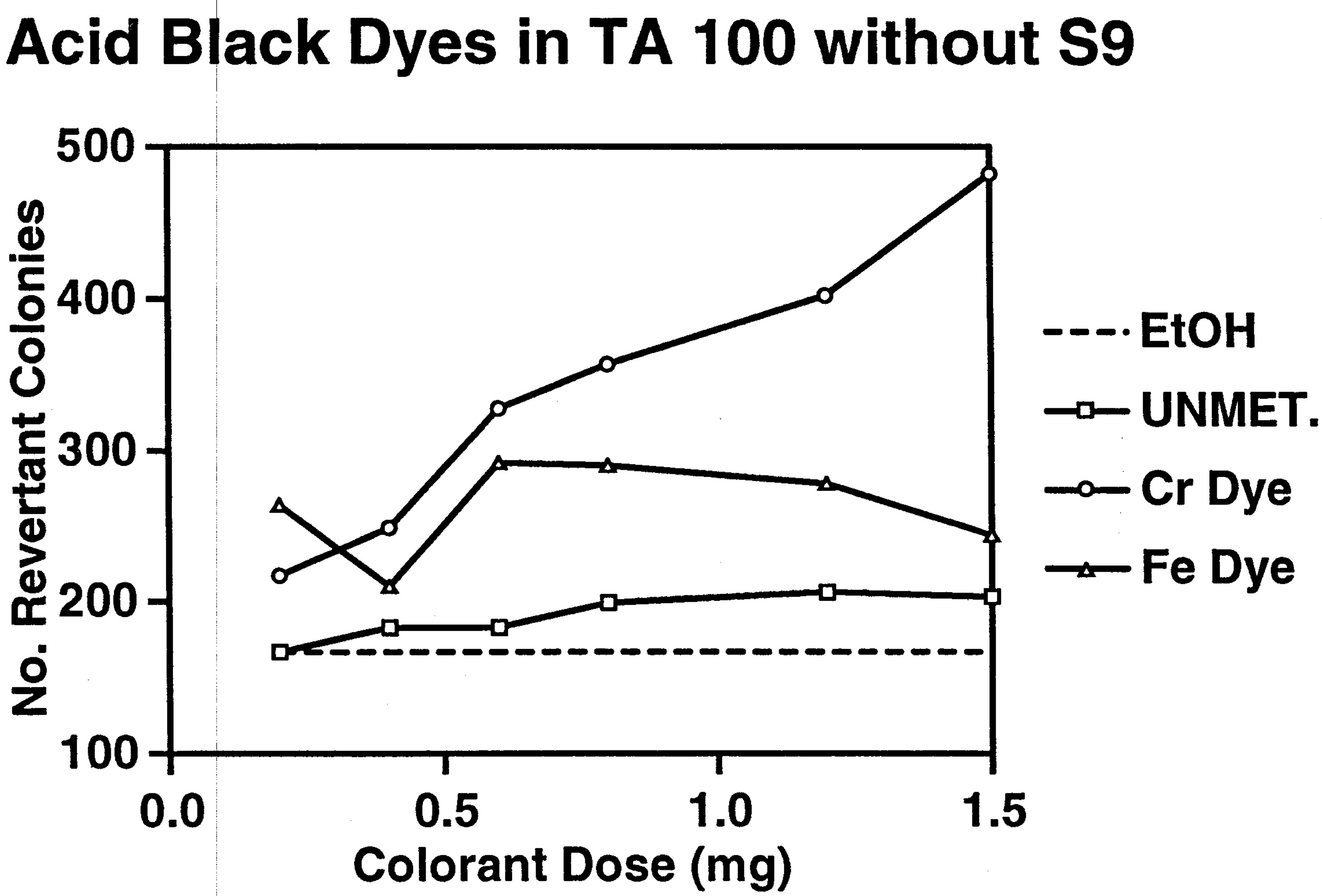


Figure 1. Ames mutagenicity data from the evaluation of Dye VII without metabolic activation. (dashed line = control; triangle = dye VII; circle = Acid Black 172; square = unmetallized dye).

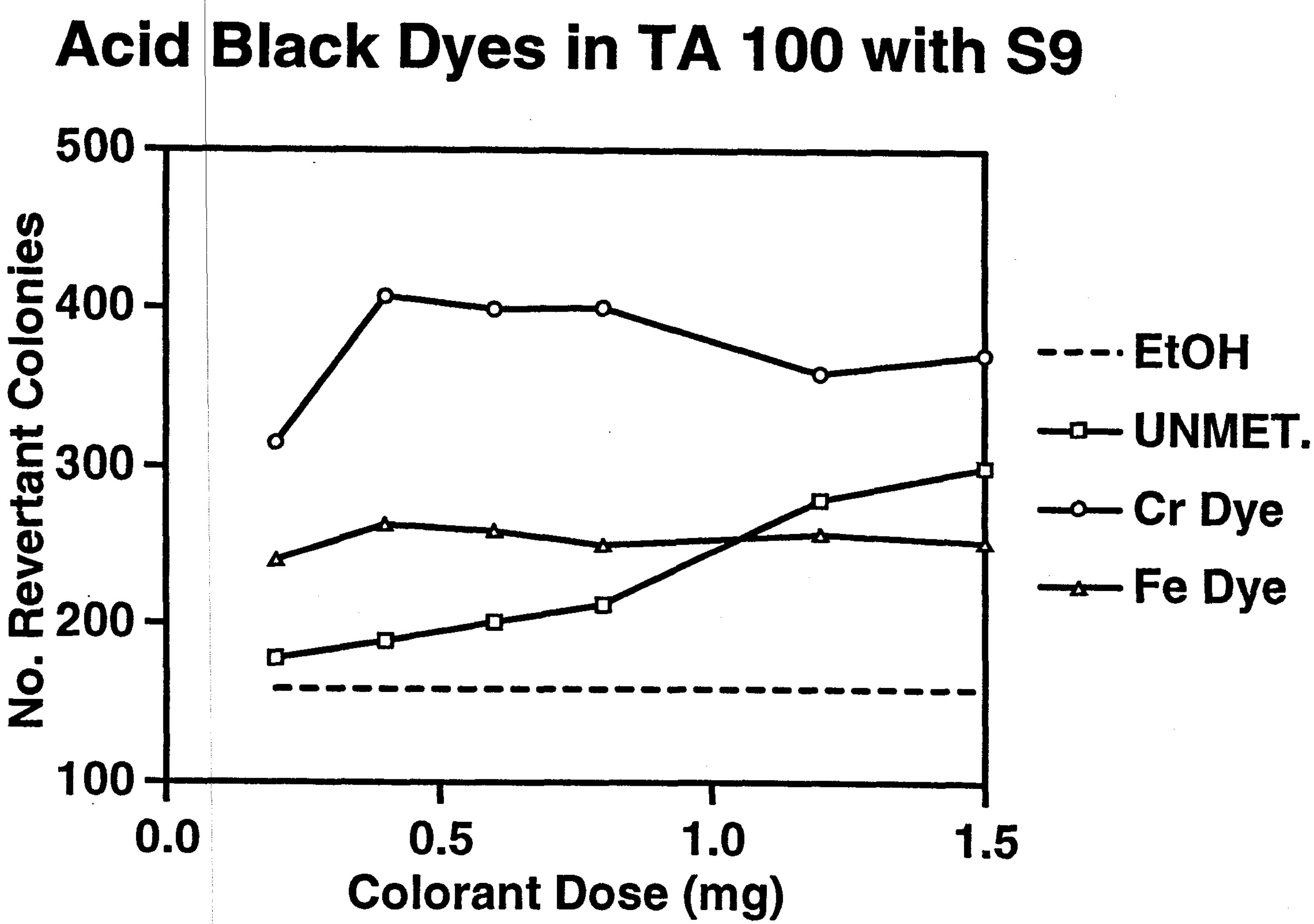


Figure 2. Ames mutagenicity data from the evaluation of Dye VII in TA100 with metabolic activation. (dashed line = control; triangle = dye VII; circle = Acid Black 172; square = unmetallized dye).

Future Work

With the recent purchase of two molecular modeling systems, we are poised to pursue objective #3 of this research program. The approach we have in mind utilizes MO-based computational chemistry to define the nature of the LUMO and HOMO of organic compounds. We will employ ZINDO calculations, in focusing on metallized dyes. We also believe that the docking feature of one of these system will enable us to model dye-DNA interactions, which should prove useful in enhancing our understanding of the mechanism(s) of dye genotoxicity.

References For Further Information

1. J. Sokolowska-Gajda, H. Freeman, and A. Reife, *Synthetic Dyes Based On Environmental Considerations: 1) Iron Complexes for Protein and Polyamide Fibers*, Textile Res. J., **64**(7), 388 (1994).

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4. J. Sokolowska-Gajda, H. Freeman, and A. Reife, *Chemical Removal of Phosphate Ions from Disperse Dye Filtrates*, in A. Reife and H.S. Freeman eds., The Environmental Chemistry of Dyes and Pigments, John Wiley & Sons, in press.